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A Study of the Mechanism of the Degradation of Cellulose by Vibratory Grinding

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A STUDY OF THE MECHANISM OF THE DEGRADATION OF CELLULOSE BY VIBRATORY GRINDING

A thesis submitted by

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INTRODUCTION

THE CONCEPT OF A MECHANICOCHEMICAL MECHANISM OF POLYMER DEGRADATION

Numerous studies have shown that a mechanical strain imposed on a polymer system may result in significant decreases in the experimentally determined molecular weight of the polymer. Examples of mechanically induced polymer degradations include mastication of polymers brought into the rubbery state by solvent addition or heating; ultrasonic and sonic vibration, turbulent flow, laminar flow, shaking, and high-speed stirring of polymers in solution; and milling of polymers in the solid state.

An important theoretical question that arises for all these mechanical polymer degradations is whether they are characterized by actual mechanical rupture of primary bonds or whether the mechanical energy must first be dissipated as heat to cause secondary oxidation, thermal, or hydrolysis reactions. Another important theoretical question arises concerning the nature of the chemical reactions involved in the polymer chain scission. These questions will be discussed from an over-all viewpoint with several types of mechanically strained polymer systems being considered.

Staudinger and Heuer (1), in studying the degradation of solid polystyrene by ball-milling and of polystyrene in solution by turbulent flow through a platinum nozzle, first visualized the mechanical degradation of a polymer to be the result of actual mechanical rupture of primary carbon-carbon bonds in the polymer backbone. Kauzmann and Eyring (2), in commenting on the degradation of rubber during cold mastication, expressed this concept more specifically as the homolytic cleavage of carbon-carbon bonds with two free radicals being formed at each chain break.

Several early experimental investigations and theoretical analyses tended to confirm the idea that polymer degradations could be mechanical in origin. Hess, Steurer, and Fromm (3) have considered the kinematics within a rocking mill. Making the assumption that only 1-2% of the pressure surfaces between the balls is coated with the material being ground, they have shown that the stresses exerted on the polymer are of sufficient magnitude to rupture chemical bonds mechanically. Morris and Schnurman (4) calculated the rate of shear necessary to rupture a central bond of a hydrocarbon polymer in solution under conditions of laminar flow. Experimental evidence confirmed the calculated order of magnitude for the critical value of the rate of shear at which degradation could occur as a function of chain length.

Hess, Steurer, and Fromm (5) have determined the temperature coefficient for the mechanical degradation of cellulose by ball-milling. Since hydrolytic and oxidative degradations of cellulose exhibit quite a large temperature dependence but the mechanical degradation showed virtually no temperature dependence, they concluded that the degradation was strictly mechanical.

Hess and Steurer (6) have considered the possibility that a thermal degradation occurs during ball-milling cellulose. Since the over-all temperature rise during grinding did not exceed 12°C. at temperature equilibrium and since the carbon content did not increase with time, as occurs in thermal degradations, but remained constant, they concluded that degradation due to heating of the whole grinding mass did not occur. They did not, however, exclude the possibility of local heating to high temperature at the place of impact but estimated this temperature using the previously determined kinetic energy of the balls (3) and the volume subject to impact. The calculated temperature rise was about 46°C., insufficient to cause thermal reactions. The temperature at the point of impact

was also estimated by the continuous grinding of maleic acid crystals. At a temperature of about 130°C., maleic acid is converted to fumaric acid. Since grinding for 600 hours yielded no fumaric acid, the temperature at the point of impact was assumed less than 130°C., insufficient to cause serious thermal degradation.

The mechanism proposed by Kauzmann and Eyring to account for the degradation of rubber by cold mastication in air was finally verified by the work of Pike and Watson (7) and Ayrey, Moore, and Watson (8). In the first investigation, it was shown that small amounts of a large number of substances likely to react with free radicals greatly accelerated the rate of degradation of rubber during mastication under nitrogen. In the second investigation, rubber was masticated under nitrogen in the presence of the radical-acceptors 1,1'-diphenyl-2-picryl hydrazyl (DPPH) and [S^{35}]-labeled 1,1'-dinaphthyl disulfide and the amount of radical-acceptor consumed during mastication was quantitatively determined. In both cases, the decrease in the molecular weight of the rubber and the amount of radical-acceptor consumed during grinding agreed with that predicted if two free radicals were formed at each chain break.

More recently, numerous studies have demonstrated that mechanical rupture of molecules to form free radicals occurs very widely among polymers. For example, Ceresa and Watson (9) have masticated polymethyl methacrylate, cellulose acetate, polystyrene, and polyvinyl acetate brought into rubbery state by solvent addition and have shown that the presence of a radical-acceptor accelerates the degradation. Using DPPH as a radical scavenger, Henglein (10) has shown that the ultrasonic degradation of a polymethyl methacrylate solution proceeds mechanically with two free radicals formed at each chain break. Thomas (11) has used DPPH to accept free radicals formed by the sonic degradation of polyisobutene, polylauryl methacrylate, and polystyrene solutions.

Johnson (12) has studied the degradation of polyisobutylene and polystyrene using iodine as a radical scavenger and has shown that degradation proceeds via Kauzmann and Eyring's mechanicochemical mechanism.

Using electron spin resonance techniques, Bresler, et al. (31) have established the presence of free radicals in a number of polymer samples that were mechanically degraded by milling. These polymer samples were characterized by the fact that they possessed only carbon-carbon bonds along the polymer backbone.

Berlin (13) has perceived that mechanical degradations may also be capable of causing heterolytic scission in many polymers and minerals. He states that the chemical properties of the macromolecules, the physical state in which they are degraded, and the medium in which they are degraded are important factors in determining whether homolytic or heterolytic cleavage of bonds occurs during mechanical degradation. Little work has been reported in this area although Berlin and Dubinskaya (14) have investigated the degradation of polydimethylsiloxane ($[SiO(CH_3)_2]_n$) solutions by ultrasonic waves and have found that organic radical-acceptors and iodine are not consumed even though the polymer is degraded. Ceresa (15) also reports that current investigations indicate that heterolytic, mechanical scission can occur alongside homolytic scission with certain polymers to initiate ionic, block copolymerizations. No information as to the types of polymers used is available.

It is of interest to note that, for a given set of conditions, a limiting molecular weight is obtained for polymers that have been degraded strictly by mechanical means. [See for example (1, 9, 38).] It is also observed that as the molecular weight of the degraded polymer approaches this limiting molecular weight, the rate of degradation is significantly decreased. These observations have been

explained on the basis that only bonds in the central sections of the polymer more than a certain distance from the ends of the molecule suffer rupture. Molecules not large enough to possess central sections with sufficiently large terminal ends do not accumulate bond-dissociation energy from the applied mechanical shear stress. Thus, mechanical polymer degradations tend to produce a more uniform distribution of polymer molecular weights from heterodisperse samples.

An example of another type of mechanicochemical mechanism for the degradation of polymers is provided by the work of Kuz'minskii, et al. (16), who have studied the oxidative degradation of a mechanically fatigued styrene-butadiene vulcanizate at two different temperatures. It was found that, at a given temperature, the rate of oxidative degradation was significantly higher for the stressed polymer than for the unstressed polymer. Mechanical fatigue at this temperature did not cause degradation except in the presence of oxygen. It was also found that the activation energy for the oxidation reaction was decreased by mechanical stress and from this it was concluded that mechanical energy can supply part of the activation energy for the oxidative degradation of polymers. Mullins and Watson (17), have verified these findings by observing that the oxidative degradation of rubber is markedly accelerated by mastication.

Therefore, there exists a range of reaction types in which mechanical work and thermal energy in different relative proportions provide the required activation energy for polymer degradation. The chain scission reaction involves a bimolecular reaction in which reactive sites on the polymer backbone are in part activated mechanically to the necessary energy level for the chain scission reaction to occur. This energy level is well below the bond dissociation energy level. Such a degradation mechanism differs markedly from the mechanicochemical degradations previously discussed which involved molecular dissociations with the

energy of dissociation being produced predominantly by mechanical work. This type of degradation is formally similar to unimolecular thermal dissociations.

THE MECHANISM OF THE DEGRADATION OF CELLULOSE BY GRINDING

The mechanism of the degradation of cellulose by ball-milling has been the subject of conflicting theories since the degradation was first observed by Waentig (18) in 1921. Meyer (19) states, "While it is true that in many technical processes involving mechanical treatment (such as vigorous wet beating) cellulose is broken down, it appears to us more probable that this is primarily a chemical hydrolysis resulting from oxidation by air or by the action of hydrogen ions and that mechanical rupture of the chain (which may be produced in fibers under tension) does not occur, or does so only to a very limited extent." McBurney (20), however, states, "The most likely explanation appears to be that this type of degradation is strictly a mechanical effect." To date, this controversy is still unresolved.

The preponderance of experimental evidence accumulated to date strongly suggests that the mechanical degradation of cellulose by ball-milling is completely mechanical in origin. It is known that the mechanical stresses in a ball mill are sufficiently large to degrade polymers having carbon-carbon bonds in the polymer backbone. The work of Bresler, et al. (31) indicates that such degradations occur mechanically with homolytic cleavage of primary bonds. Thus, a mechanically activated hydrolysis or oxidation reaction of cellulose with only part of the activation energy coming from the mechanical work appears unlikely because the stresses in the ball mill are sufficiently large to actually rupture chemical bonds.

This conclusion is verified by the work of Hess, Steurer, and Fromm (5), who have shown that the temperature coefficient for the degradation of cellulose by

grinding is practically zero. Also supporting this conclusion is the work of Assarson, et al. (21), who have analyzed the end groups present in ball-milled cellulose by borohydride reduction, hydrolysis, and isolation of the glycitols present in the hydrolyzate. Glucitol, arabitol, and erythritol (10:3:2 by weight) were found. The apparent chain scission by rupture of chemical bonds within the rings is indicative of high shear stresses on the polymer during ball-milling.

Whether the degradation is characterized by macroradical or macroion formation at each chain break is less easily resolved. It is thought that the nature of the unstressed bonds that are ruptured, i.e., whether they tend to be more covalent than ionic or vice versa, may be an important factor in determining whether heterolytic or homolytic chain scission occurs. However, if we consider that bond rupture occurs according to the mechanism proposed by Bestul (23), it is conceivable that factors other than the equilibrium arrangement of electrons are involved. Bestul visualizes that portions of the mechanical energy applied to a polymer system which cause inter- and intramolecular motion are temporarily stored as potential energy in chemical bonds during the finite times required for these motions. It is thought that this stored mechanical energy alters the equilibrium position about which the bonded chain atoms vibrate thermally. If sufficient potential energy is introduced into a bond in addition to its thermal energy, the binding energy may be overcome and bond rupture occurs.

There is good experimental evidence that macroradicals are formed when cellulose is mechanically degraded. It has been observed that when ethyl cellulose is masticated in the presence of several vinyl monomers, the monomers are polymerized (53). For a given monomer, the mastication time required to reach a given level of monomer conversion is very nearly the same for ethyl cellulose and a number of other polymers containing carbon-carbon bonds in the polymer backbone. A patent

issued to N. V. de Battafsche (24) indicates that when cellulose or cellulose derivatives are ground in the presence of vinyl monomers, the monomers are polymerized. These investigations, together with the work of Ceresa and Watson (9), who have observed that the presence of an organic radical-acceptor speeds the degradation of cellulose acetate during mastication, indicate that macroradicals are formed during the grinding of cellulose.

Also indicating that macroradicals are formed during the grinding of cellulose is the observation that the rate of degradation during ball-milling is higher in an oxygen atmosphere than in a carbon dioxide atmosphere (25). Oxygen is known to be an effective radical scavenger. These results, however, contradict the results of Grohn (26), who has found that there is no effect on the rate of cellulose degradation whether it is ground under oxygen or nitrogen.

Grohn also has noted a linear increase of the copper number with the degree of rupture measured by 1/DP and has concluded that since one carbonyl group is formed for each chain break, the degradation is ionic. However, it should be noted that alkoxy and peroxy types of free radicals are known to decompose giving aldehydes and ketones as final products (27).

The similarity between the mechanical degradation of polymers and formally unimolecular thermal or photolytic dissociation has already been noted. It is of interest, then, that photolysis of organic esters and pyrolysis of ethers provide an excellent source of alkoxy and alkyl radicals by rupture of carbon-to-oxygen bonds (22). While no complete investigation using acetals has been reported, it appears likely that either photolysis or pyrolysis of them will generate alkoxy radicals because bond strength data indicates that the degree of covalency of the carbon-oxygen bond in an acetal is virtually the same as that in an ester or ether

(22). This suggests that the carbon-oxygen glycosidic link in cellulose is sufficiently covalent to form free radicals on mechanical rupture.

THE PURPOSE AND SCOPE OF THE PRESENT INVESTIGATION

The preliminary phases of the work presented in this thesis were undertaken to confirm the theory that free radicals are formed during the ball-milling of cellulose. One technique employed to detect macroradicals in a ball-milled cellulose sample was the use of electron spin resonance (ESR). Since the theory and experimental techniques involved in organic free radical detection using ESR are comprehensively covered in review by Wertz (29) and Wiffen (28, 30), there appears little need to discuss them in detail here. The following remarks will be helpful in understanding the nature of the experiment, however.

The electronic angular momentum of an organic free radical arises only from the uncoupled spin of the free electron; there is no orbital contribution to the paramagnetism. When organic free radicals are placed in a strong magnetic field, H, splitting of their spin angular momentum into two energy levels occurs. These energy levels are given by $g\mu_B MH$ where g is the Lande or spectroscopic splitting factor, μ_B is the Bohr magneton, and M is the magnetic quantum number which has values $\pm 1/2$.

If a radiofrequency alternating magnetic field is now applied at right angles to the strong magnetic field, transitions between the two energy levels occur. In a system at temperature equilibrium with its surroundings, the state of lower energy has the greater population and transitions from this state occur more often than transitions from the upper state. The result is that energy from the radiofrequency field is absorbed and there is a shift toward a more equal distribution in the two levels. The absorption of energy is a maximum under the conditions for

resonance, i.e., when the frequency of the oscillating field, γ, coincides with the natural frequency between the two levels. The resonance condition is expressed by

$$h\gamma = g\mu_B \Delta MH = g\mu_B H$$

where h is Plank's constant. The free electron value for g, i.e., the value for zero orbital magnetic moment, is 2.0023. Many organic free radicals give g-values equal to or very nearly equal to the free-electron value (29). Resonant frequencies for free radical samples in fields of the kilogauss range will be in the microwave (kilomegacycle) region.

Provided transition or rare earth elements, ionic crystals which contain lattice imperfections, or alkali metals in liquid ammonia are not present, the existence of an electron spin resonance spectrum can be considered conclusive proof of the existence of free radicals. Therefore, ESR is especially well suited for studying polymer free radicals because the interfering substances mentioned above are rarely encountered and because the radicals are selectively examined in the presence of other molecules.

At least one paper dealing with the ESR spectra determinations for mechanically degraded polymers has been published. Bresler, et al. (31) have reported and discussed ESR spectra for several mechanically disrupted polymers including polymethyl methacrylate, polystyrene, and polyethylene. Degradations were conducted by milling the polymers in a specially constructed, hermetically sealed chamber under liquid nitrogen containing 10% oxygen and in vacuo. Under some conditions, the macroradicals gave observable spectra at least an hour after milling. From this work, it appeared likely that macroradicals present in ball-milled cellulose samples could be detected using ESR provided they were present in sufficient quantities.

The other technique used to detect the formation of free radicals during the grinding of cellulose was the incorporation of a radical scavenger in the grinding system. Chemical reaction of the radical scavenger with cellulose being mechanically degraded by ball-milling may be considered strong evidence that free radicals are formed during the grinding. Preliminary work using 2,4,6-triphenylphenyl peroxide and diphenyl picryl hydrazyl as radical scavengers indicated that these acceptors were too unstable in the grinding system to give meaningful results. Because of this, iodine containing a small amount of iodine-131 was employed to confirm the observation that free radicals are formed during the ball-milling of cellulose.

Once it had been established that free radicals were formed during the grinding of cellulose, major interest was centered around the extent to which a mechanically initiated, free radical degradation mechanism plays a part in the degradation of cellulose by grinding. If $\underline{\overline{DP}}_{no}$ is the initial number average molecular weight of a cellulose sample and $\underline{\overline{DP}}_{ng}$ is the number average molecular weight after grinding, then the number of new moles formed during grinding per gram of cellulose is $1/162(1/\underline{\overline{DP}}_{ng} - 1/\underline{\overline{DP}}_{no})$. Assuming that chain scission occurs primarily at the glycosidic links with two free radicals formed for each chain break, two atoms of iodine will be consumed for every new molecule of cellulose formed during grinding provided the iodine is an effective scavenger for the cellulosic macroradicals.

Experiments involving the use of iodine as a radical scavenger were designed in an attempt to obtain semiquantitative estimates of the number of free radicals formed during grinding for comparison with theoretical estimates obtained from molecular weight determinations. Small amounts of iodine-131 have been used to provide a radiochemical method of analysis.

Some work directed toward establishing the chemical nature of one of the free radical species formed during the grinding of cellulose was also undertaken in this thesis. Assuming that chain scission occurs primarily at a glycosidic link with the formation of two free radicals, an alkoxy ($R_3C\text{-}O\cdot$) free radical will probably be formed.

It has been reported that no organic hypoiodite is stable (33) and thus reaction of iodine with an alkoxy radical to give a stable product (R_3COI) should not be expected. However, compounds of the type R_3COI may be formed *in situ* (33, 34) and in the presence of a given organic solvent, this type of structure may characteristically halogenate the solvent.

In cyclohexane, it is anticipated that cyclohexyl iodide will be formed after the reaction of iodine with an alkoxy radical; in toluene, it is anticipated that benzyl iodide will be formed (33). Identification of cyclohexyl iodide and benzyl iodide in the solvent after grinding with iodine in cyclohexane and toluene may be considered indirect chemical evidence that alkoxy radicals are formed during the mechanical degradation of cellulose.

EXPERIMENTAL

ELECTRON SPIN RESONANCE SPECTROSCOPY OF A BALL-MILLED CELLULOSE SAMPLE

APPARATUS

The Vibratory Ball Mill

The vibratory ball mill constructed by Busche (37) in accordance with specifications of the National Bureau of Standards mill (38) was employed. The brief description which follows is abstracted largely from Busche's thesis.

The mill consists of a horizontal shaft connected by means of reinforced rubber tubing to a 1/4-horsepower, 1800 r.p.m. electric motor at one end and to an eccentric weight which rotates in a housing suspended from leaf springs at the other end. A cylindrical jar of approximately one-liter capacity, surrounded by a concentric cooling chamber of the same capacity, fits into a holder which is fastened to a slip ring. The slip ring is held by the housing in such a way that the operation of the mill causes the entire assembly consisting of the ring, cooling chamber, and holder to rotate at about 4 r.p.m. about an axis coincident with the center line of the horizontal shaft. This eliminates any tendency for the material being ground to settle in the jar and thus promotes more uniform and rapid grinding. The vibratory movement of the jar assembly and housing is brought about by the rotation of the eccentric weight. This sets the stainless steel balls within the jar into rapid motion and collisions between them mechanically grinds the sample in the jar. The jar and cover were machined from 440-F stainless steel, a heat-treatable material which can be hardened to Rockwell "C" 59. 440-F, 1/4-inch stainless steel balls of the same material and hardness were used to minimize surface attrition of the balls.

The Electron Spin Resonance Spectrometer

The Varian spectrometer at the Institute of Enzyme Research in Madison, Wisconsin, was employed. The magnet in this instrument had a 6-inch pole diameter and a field strength of 3300 gauss.

REAGENTS

High-viscosity, acetate-grade cotton linters (Type 1-AR-2300) supplied by Buckeye Cellulose Corporation in sheet form were used. Approximately 1500 g. were ground in a Wiley mill to pass through a plate having 0.040-inch diameter holes and the sample was stored in a humidity room at 72°F. and 50% R.H. Degree of polymerization and degree of polymerization distribution data on this cellulose sample may be found in Appendix I.

PROCEDURES

Ball-Milled Cellulose Sample Preparation

The grinding jar was charged with 5 grams of airdry cellulose and 2800 grams of stainless steel balls under a nitrogen atmosphere and the jar cover put in place. The area between the jar and jar cover was sealed with molten microcrystalline wax, and the cellulose sample ground for 36 hr. After grinding, the jar was opened under nitrogen and a cellulose sample, separated from the balls by screening, was transferred to a 3-mm. inside diameter pyrex tube; the tube was sealed and placed in a Dewar flask containing dry ice for transportation to Madison.

Electron Spin Resonance Spectra Determinations

Electron spin resonance (ESR) spectra were determined using a phase-sensitive detection technique by which the 3-cm. microwave is modulated at a frequency of

100 kc.p.s. with an amplitude which is small compared to the line width of the signal. As the main magnetic field was varied, a pen recorder plotted the first derivative of the radio-frequency power absorbed by the sample with respect to the main field strength as a function of the magnetic field strength. Measurements were made at a temperature of 120°K. some four or five hours after grinding.

When the spectrum of the ball-milled cellulose sample in the pyrex tube was determined, it was found that the tube itself exhibited considerable paramagnetic absorption. Therefore, the sample was transferred to a thin-wall quartz tube which does not absorb energy from the radio-frequency field. During the transfer, the sample was exposed to atmospheric oxygen. In addition to the spectrum for the ball-milled cellulose sample, spectra were determined for the empty quartz tube and a cellulose sample that had been ground and allowed to stand for several days.

THE MECHANICAL DEGRADATION OF CELLULOSE BY GRINDING IN THE ABSENCE AND PRESENCE OF IODINE

APPARATUS

The vibratory ball mill previously described was used in all experiments. To prevent leakage of solvent from the ball mill, the area between the jar and jar cover was fitted with a polyethylene gasket. All runs were made with the ball mill in a 4°C. cold room. The equilibrium temperature reached during grinding was about 14°C.

For counting radiation, a Tracerlab model TGC-5 self-quenching Geiger tube connected to a Berkeley model 2000 decimal scaler was employed. Counts obtained using this equipment represent about 0.1% of the disintegrations due to beta and gamma irradiation.

For analyzing the solvent after grinding, an Aerograph model 110-C gas chromatograph with a carbowax 20 M (a polyethylene glycol) column was employed. This instrument has a thermal conductivity detector which contains four heated filaments--two reference and two sensing. Helium passes through the reference side before entering the column and then through the detector side after emerging from the column. Thermal conductivities were recorded by a Minneapolis-Honeywell model 143x58 high-speed recorder.

Ultraviolet spectra and iodine concentration determinations were made with a Beckman model DU spectrophotometer. One-cm. silica or Corex cells containing about three milliliters of solution were used.

Cellulose viscosities were measured using a Cannon-type dilution viscometer. All measurements were made in a constant temperature bath held at 25 $\pm$ 0.06°C.

REAGENTS

Cellulose

The acetate-grade cotton linters previously described were used in all experiments.

Solvents

Practical-grade cyclohexane was washed three times with concentrated sulfuric acid and once with water, dried with calcium chloride and distilled. The product was treated with silica gel prior to use.

Distilled, spectral-grade carbon tetrachloride and distilled, reagent-grade toluene were used.

For cellulose viscosity determinations, Ecusta 1.0M cupriethylenediamine diluted volumetrically to 0.5M was employed.

Iodine and Sodium Radioiodide I-131

Baker reagent-grade iodine was used in all cases. Sodium radioiodide I-131 was supplied by the Volk Radiochemical Company in 2- or 3-millicurie lots.

Other Reagents

The sulfuric acid and dextrose used were of analyzed reagent grade.

One-molar sodium thiosulfate solutions were prepared by dissolving weighed amounts of reagent-grade $Na_2S_2O_3 \cdot 5H_2O$ into distilled water.

Both Mathieson prepurified nitrogen and water-pumped nitrogen supplied by the National Cylinder Gas Company were used.

PROCEDURES

Sodium Radioiodide-Iodine Radiation Exchange

The aqueous sodium radioiodide solution containing two or three millicuries of iodine-131 was diluted to about 5 ml. and placed in a 50-ml. extraction funnel fitted with a Teflon stopcock. About 20 ml. of a carbon tetrachloride or cyclohexane solution containing 10 grams of iodine per liter was then added and the exchange effected by moderate agitation of the funnel. The organic layer was collected by filtration through a dry cotton plug. The exchange was repeated three or four times with additional 20-ml. portions of iodine solution. Well over 90% of the radioactivity was transferred to the iodine by this method.

After the exchange had been completed, the iodine solution was dried with calcium chloride and stored for future use.

Preparation of Cyclohexyl Iodide

Cyclohexyl iodide was prepared by the method of Stone and Schechter (35). Forty-one grams of cyclohexene (practical grade) were added to a mixture of 250 g. of potassium iodide in 221 g. of 95% phosphoric acid. The 95% phosphoric acid was prepared by adding 47 g. of phosphorus pentoxide to 174 g. of 85% phosphoric acid. After being heated for three hours at 80°C., the mixture was added to about a liter of water and the organic layer was separated, washed twice with water and dried with calcium chloride.

The product was distilled and the distillate boiling between 175 and 193°C. was collected. The product was then redistilled and the distillate boiling between 190 and 192°C. was collected. This product was decolorized by shaking with water and a few sodium hydroxide pellets, washed with water, and dried with calcium chloride. The refractive index of the product was 1.546. Literature values of 1.549, 1.551, and 1.547 have been reported (36).

Preparation of Benzyl Iodide

Benzyl iodide was prepared according to the method of Coleman and Hauser (42). Sixty-three grams of benzyl chloride were added to 100 g. of sodium iodide in 500 ml. of dry acetone and the mixture was refluxed for 1 hour. The mixture was then poured into 1500 ml. of water and the oil that separated was placed in a freezing compartment until solidified. The solid was recrystallized three times from absolute ethanol to give a product which melted at 21°C. [24°C. reported (42).] After extracting the melted product with aqueous sodium thiosulfate to remove the last traces of free iodine, the product was dried with calcium chloride, dissolved in four times its volume of toluene, and stored in the dark at -10°C.

Correlation of Molecular Weight Loss and Grinding Time for the Mechanical Degradation of Cellulose in the Presence of Cyclohexane

Prepurified nitrogen was bubbled through 300 ml. of cyclohexane and the cyclohexane along with 2250 g. of stainless steel balls and 5.29 g. of airdry cellulose was placed in the grinding jar under a stream of nitrogen. The jar was then thoroughly flushed with nitrogen, the jar cover gasket and cover were put in place, and the jar was sealed. The jar assembly was then bolted to the ball mill housing and the cellulose was ground for the desired length of time. Three runs varying from 18 to 29 hours were made. After each run, the sample was collected by filtering the slurry through filter paper.

Three runs were also made using a dried cellulose prepared as follows. A 5.29-g. portion of airdry cellulose was dried at 105°C. for about three hours. It was then quickly transferred to a 250-ml. Erlenmeyer flask with a ground-glass stopper and about 100 ml. of absolute ethanol was immediately added. After standing overnight, the alcohol was filtered off and the sample was again dried for about 3 hours at 105°C. The sample was once again transferred to the Erlenmeyer flask and about 100 ml. of cyclohexane were added. Prior to use, the cyclohexane was removed by filtration and the sample was again dried for 3 hours at 105°C. The jar was then charged with the cellulose sample directly from the oven, the cyclohexane, and the balls and the procedure previously described was repeated.

After grinding, the molecular weights of the samples were determined. About 0.2 g. of sample was placed in a small weighing bottle, dried at 105°C. for about 3 hours, and weighed directly into a 50-ml. volumetric flask. The flask was then about two-thirds filled with 0.5M cupriethylenediamine and agitated until the

sample had dissolved. The flask was then diluted to volume. The specific viscosity, η_{sp}, was determined as a function of concentration at 25°C. using a Cannon dilution viscometer. Eight milliliters of the original solution were used and 4 ml. of 0.5M cupriethylenediamine were used for each dilution. The solvent time for the viscometer used was about 300 sec. Kinetic energy corrections were shown to be small.

The intrinsic viscosity, $[\eta]$, was obtained by extrapolating the plot of $\log \eta_{sp}/c$ vs. c to zero concentration according to the Martin equation:

$$\log (\eta_{sp}/c) = \log [\eta] + K[\eta]c$$

where

η_{sp} = specific viscosity = $t/t_o - 1$

t = solution time through the viscometer

t_o = solvent time through the viscometer

$[\eta]$ = intrinsic viscosity

K = constant, and

c = concentration, g./100 ml.

Number average molecular weights were obtained from the intrinsic viscosity using the correlation of Immergut, et al. (39).

$$[\eta] = 1.33 \times 10^{-4} M^{0.905}$$

where

$[\eta]$ = intrinsic viscosity, dl./g., and

M = number average molecular weight

Correlation of Molecular Weight Loss, Grinding Time, and Iodine Uptake for the Mechanical Degradation of Cellulose in the Presence of an Iodine-Carbon Tetrachloride Solution

Proper amounts of the radioiodine-iodine-carbon tetrachloride solution, a stock carbon tetrachloride solution containing 2 g. of iodine per liter, and carbon tetrachloride were mixed together to give 350 ml. of a solution which contained about 0.1 g. of iodine per liter and enough radioiodine to give a count of from 10,000 to 20,000 counts per minute (c.p.m.). Water-pumped nitrogen was then bubbled through this solution for 5 or 10 minutes and a portion was removed for spectrophotometric determination of iodine content (see Appendix II).

Three hundred milliliters of this solution along with 5.29 grams of airdry cellulose (5 g. ovendry) and 2250 grams of stainless steel balls were charged into the grinding jar under nitrogen. After thoroughly flushing the jar with nitrogen, the cover gasket and cover were put in place and the jar was sealed. The jar was then bolted to the ball mill housing and the contents ground for the desired length of time. Five different runs of from 12 to 34 hours were made.

After grinding, the slurry was separated from the balls by filtering through a coarse wire screen and the volume recovered was measured. The slurry was then diluted to 300 ml. with carbon tetrachloride and counted in a 400-ml. tall beaker using the dip counter. All counts were made with the counter immersed to the same depth in the center of the beaker. During the count, the slurry was stirred magnetically. The time required to give 10,000 counts was recorded.

After counting, the slurry was filtered on a 40-mm. coarse, sintered-glass filter and about 0.6 g. of the ground cellulose was removed for a viscosity determination. The remainder was placed in a 250-ml. Erlenmeyer flask and dispersed in about 75 ml. of carbon tetrachloride. One hundred milliliters of 65% sulfuric acid

was added as the slurry was stirred magnetically. Stirring was continued until the cellulose had completely dissolved in the sulfuric acid.

When the ground cellulose had been completely dissolved, the mixture was transferred to a 500-ml. extraction funnel and the sulfuric acid layer was shaken with successive portions of carbon tetrachloride until there was no visual evidence that free iodine was still being removed in the carbon tetrachloride layer. The sulfuric acid layer was then extracted two more times with carbon tetrachloride. The carbon tetrachloride fractions used for extraction were collected for further analysis.

The sulfuric acid layer was diluted to 300 ml. with distilled water and counted just as before. A minimum of five 100-second counts were made and the results averaged. One-hundred-second background counts on 300 ml. of distilled water were also made.

After determining the total volume, about 400 ml. of the carbon tetrachloride used for the free iodine extraction was extracted three times with 1M sodium thiosulfate and dried with calcium chloride. Three hundred milliliters was then counted at least five times for 100 seconds and the results averaged. One-hundred-second background counts on carbon tetrachloride were also made and averaged.

The total viscosity sample was dried at 105°C. and weighed, and about 0.2 g. was placed in a small weighing bottle. The specific viscosity as a function of concentration, intrinsic viscosity, and molecular weight of this sample were determined as previously reported.

The iodine consumed by the cellulose during grinding was taken to be the sum of the iodine in the sulfuric acid layer that could not be extracted with carbon

tetrachloride and the iodine in the carbon tetrachloride extract that could not be extracted with sodium thiosulfate. The count in the latter phase was 20% or less of the count in the former. The fraction of the total initial free iodine that reacted with the cellulose during grinding was then equal to the ratio of counts in these two phases to the count after grinding prior to extraction since no appreciable radiochemical decay of the iodine-131 occurred during the period over which these counts were made (2 hr.). To determine iodine consumption per gram of cellulose, corrections for the cellulose unrecovered after grinding and the cellulose removed for the viscosity sample were made.

Five runs at an iodine concentration of 0.5 g. per liter and five runs at an iodine concentration of 2 g. per liter were also made. The only variation from the procedure that has been reported was that the viscosity samples were thoroughly washed with acetone prior to weighing in order to remove absorbed iodine.

Correlation of Molecular Weight Loss, Grinding Time, and Iodine Uptake for the Mechanical Degradation of Cellulose in the Presence of an Iodine-Cyclohexane Solution

Enough of the radioiodine-iodine-cyclohexane solution (0.5-3 ml.) was added to 310 ml. of stock solution containing 2 g. of iodine per liter to yield a solution giving a count of from 10,000 to 20,000 c.p.m. Prepurified nitrogen was bubbled through this solution for 5 or 10 minutes.

Three hundred milliliters of this solution along with 5.29 grams of airdry cellulose (5 g. o.d.) or 5 g. of ovendry cellulose (dried as previously described) and 2250 g. of stainless steel balls were charged into the grinding jar under a stream of prepurified nitrogen. The jar was then sealed and the cellulose ground for the desired length of time. Six runs of from 22 to 41 hours were made.

After grinding, the cellulose, cyclohexane slurry was filtered and the cellulose sample treated just as has been described for the grinding of cellulose in iodine and carbon tetrachloride. This includes extracting the excess iodine from the sulfuric acid layer with carbon tetrachloride.

Solvent Analysis After Grinding Cellulose in Cyclohexane with Iodine

The cyclohexane filtrate was collected from two runs (26 and 40 hr.) in which airdry cellulose was ground in cyclohexane containing 2 g. of iodine per liter. Each of these filtrates was extracted three times with 1M sodium thiosulfate to remove the iodine, dried with calcium chloride, diluted to 300 ml., and counted. The counts indicated that an iodine concentration of about 0.01 to 0.015 g. iodine per liter remained in the cyclohexane after thiosulfate extraction.

The combined filtrates were distilled down to a volume of about 12 ml. and 50 microliters of this solution were gas chromatographed using the carbowax column. The furnace temperature was 136°C.; the temperature of the collector was 170°C.; the temperature of the injector was 155°C.; the helium pressure was 14.5 p.s.i.g. Fifty microliters of cyclohexane and a known solution containing 5 microliters of cyclohexyl iodide per 50 ml. of cyclohexane were also chromatographed under the same conditions.

After it was noted that there was a thermal conductivity peak in the unknown comparable to what was presumed to be the cyclohexyl iodide peak in the known, the unknown solution was concentrated further to about 4 ml. and again gas chromatographed. When the recorder indicated a maximum concentration of the unknown material at the detector, the effluent gas was bubbled through cyclohexane in a 10 by 75-mm. test tube until the recorder indicated no more of the material was present in the detector cell. This procedure was repeated nine times and the

ultraviolet absorption of the collected sample was determined from 240 to 300 millimicrons using the Beckman model DU spectrophotometer. The ultraviolet spectra of two known solutions containing 3 and 5 microliters of cyclohexyl iodide in 50 ml. of cyclohexane were also determined.

Solvent Analysis After Grinding Cellulose in Toluene with Iodine

The toluene filtrate was collected from two runs (40 and 48 hr.) in which airdry cellulose was ground in toluene containing 2 g. of iodine per liter. Each of these filtrates was extracted three times with 1M sodium thiosulfate to remove the iodine, dried with calcium chloride, diluted to 300 ml., and counted. The counts indicated that an iodine concentration of about 0.01 g. of iodine per liter remained in the toluene after thiosulfate extraction.

The combined filtrates were distilled down to a volume of about 4 ml. under vacuum and 50 microliters of this unknown solution were gas chromatographed using the carbowax column. The furnace temperature was 158°C., the collector temperature 205°C., the injector temperature 190°C., and the helium pressure 14.1 p.s.i.g. Fifty microliters of toluene and a known solution containing a large quantity of benzyl iodide in toluene were also chromatographed under the same conditions.

After it was noted that there was a substance in the unknown which gave a thermal conductivity comparable to what was presumed to be the benzyl iodide peak in the known, the unknown substance was collected by combining the material from five duplicate runs in cyclohexane just as previously reported. A sample of the known benzyl iodide solution was also gas chromatographed and the iodide collected in cyclohexane. The ultraviolet spectra of the benzyl iodide and unknown compounds were determined over the range of 240 to 300 mμ using the Beckman model DU spectrophotometer.

The Reactivity of Iodine with Glucose During Grinding in Carbon Tetrachloride

Two 5-g. samples of anhydrous glucose were ground about 40 hr. in a radio-iodine-iodine-carbon tetrachloride solution containing 2 g. of iodine per liter. The procedure followed was exactly the same as that used for the grinding of cellulose in iodine and carbon tetrachloride.

After grinding, the glucose slurry was subjected to the same treatments as the cellulose except that no viscosity sample was removed. To determine if iodine reacted with the glucose, the sulfuric acid layer and the sodium thiosulfate-extracted carbon tetrachloride extract were counted as before.

The Reactivity of Iodine with Cyclohexane and Toluene During the Grinding of Glucose

Two 5-gram samples of anhydrous glucose were ground for 40 hr. in radio-iodine-iodine-cyclohexane and radioiodine-iodine-toluene solutions containing 2 grams of iodine per liter. After grinding, the cyclohexane and toluene filtrates were extracted with 1.0M sodium thiosulfate, dried with calcium chloride, and counted just as described under the solvent analysis section.

The Reactivity of Iodine with Ground Cellulose in Carbon Tetrachloride

A 5.29-gram sample of airdry cellulose was ground for 45 min. in a radio-iodine-iodine-carbon tetrachloride solution containing 2 grams of iodine per liter according to the procedure previously described. The resulting slurry was then placed in a 500-ml. Erlenmeyer with a ground-glass stopper and allowed to stand for one week.

The cellulose sample was then filtered from the slurry, dissolved in sulfuric acid and extracted with carbon tetrachloride. To determine if the iodine had

reacted with the cellulose, the sulfuric acid layers and sodium thiosulfate-extracted carbon tetrachloride extract were counted as before.

PRESENTATION AND DISCUSSION OF RESULTS

ELECTRON SPIN RESONANCE SPECTROSCOPY OF A BALL-MILLED CELLULOSE SAMPLE

The ESR spectra for the ball-milled cellulose sample appear in Fig. 1-4. Because the ESR spectra of the empty quartz tube and of a cellulose sample that had been ground eight days before showed no paramagnetic absorption, these spectra indicate the presence of at least two types of free radicals in the ball-milled cellulose sample five hours after grinding, A and B, with a possibility that a third type of radical, C, also exists.

The saturation characteristics of the two radicals, i.e., the effect of varying the power of the microwave field, can be observed in Fig. 1 and 2. The intensity of the spectrum for a radical that saturates easily will be noticeably diminished as the power of the microwave field is increased. It may be seen that the spectrum for Radical B is much more affected by the change in the power of the microwave field than is Radical A. Therefore, Radical B saturates much more readily than Radical A. No definite conclusions can be drawn from this observed effect, although it is interesting to note that Bresler, et al. (31) have observed that peroxide radicals are much harder to saturate than hydrocarbon radicals.

The effect of varying the modulation of the radiofrequency field may be seen in Fig. 3 and 4. Here the paramagnetic absorption due to copper is completely eliminated.

Values for the spectroscopic splitting factor, g, could not be determined because only the current through the magnet was recorded, and the main magnetic field strength was not known.

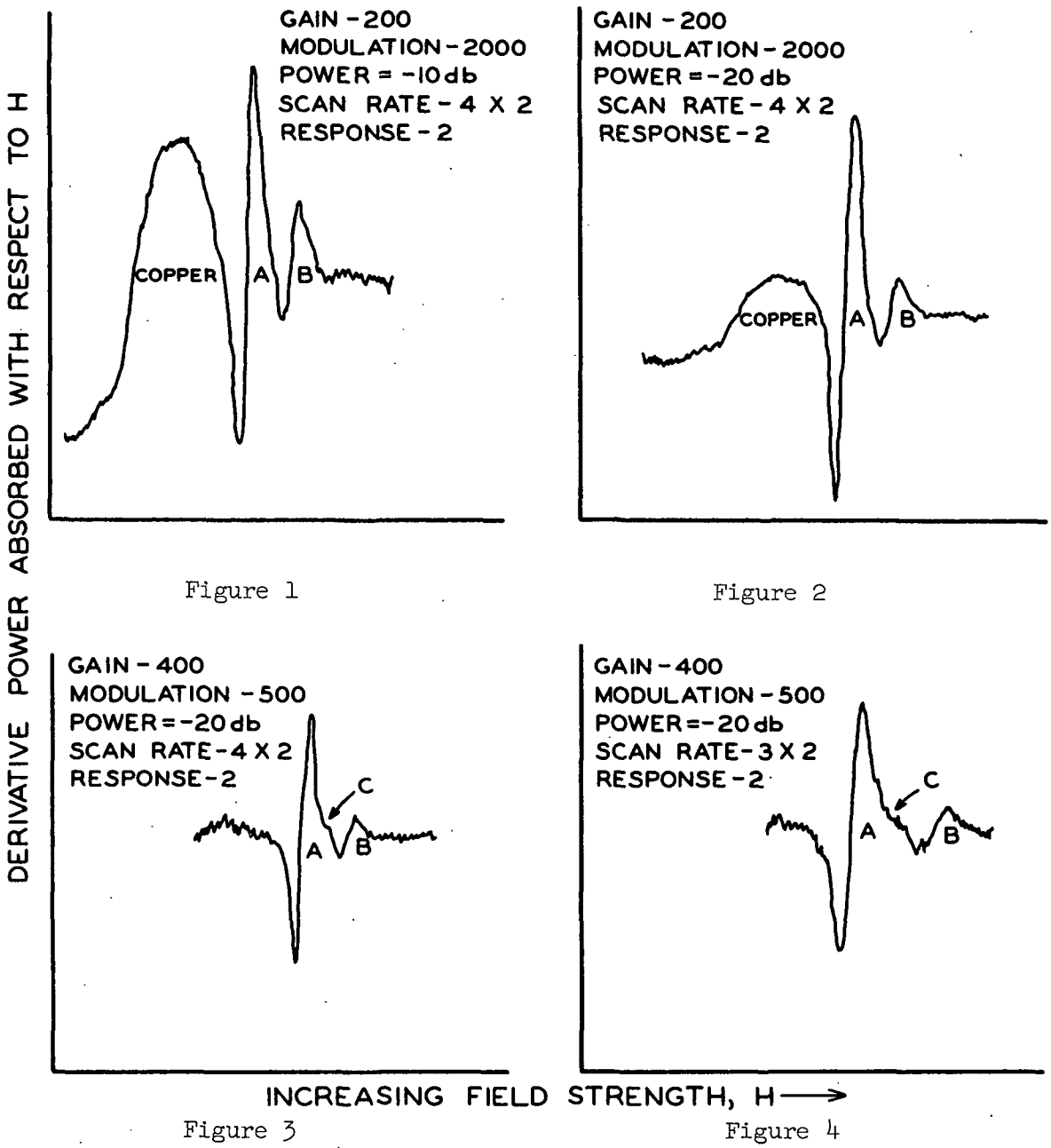

Figure 1

Figure 2

Figure 3

Figure 4

Figures 1-4. Electron Spin Resonance Spectra for a Ball-Milled Cellulose Sample

THE MECHANICAL DEGRADATION OF CELLULOSE IN THE ABSENCE AND PRESENCE OF IODINE

SUMMARY OF EXPERIMENTAL RESULTS

The results for 32 runs in which cellulose was ground in cyclohexane or carbon tetrachloride are summarized in Tables I and II. The important experimental variables for these runs were grinding time, iodine concentration in the organic solvent, and condition of the cellulose prior to grinding. After each run, iodine consumption by the cellulose was determined radiochemically and the intrinsic viscosity of the ground cellulose was determined in 0.5M cupriethylenediamine.

CELLULOSE INTRINSIC VISCOSITY AS A FUNCTION OF GRINDING TIME AND IODINE CONCENTRATION

Results from Tables I and II plotted as cellulose intrinsic viscosity versus grinding time in carbon tetrachloride and cyclohexane appear in Fig. 5 and 6. It is interesting to note that the rate of cellulose degradation is increased as the iodine concentration in carbon tetrachloride increases from 0.1 to 2.0 grams per liter and as the iodine concentration in cyclohexane increases from 0 to 2.0 grams per liter.

There are two possible explanations for this observed effect. First, the iodine may cause a secondary, chemical degradation of the cellulose, thereby only apparently increasing the rate of mechanical degradation. It is interesting to note that the same limiting intrinsic viscosity, 0.15 dl. per g., is reached when cellulose is ground for about 190 hr. in the presence and absence of iodine (Runs 19-T, 21-T, and 13-CA). This can be considered strong evidence that a chemical degradation reaction involving iodine does not occur.

TABLE I

THE GRINDING OF AIRDRY CELLULOSE IN THE PRESENCE OF IODINE IN CARBON TETRACHLORIDE

Run No.	Iodine Concentration, g./l.	Grinding Time, hr.	100 Sec. Counts on Cellulose Sample after Grinding: Total Slurry Prior to Extraction	100 Sec. Counts on Cellulose Sample after Grinding: Sample After Excess Iodine Has Been Extracted[a]	Weight of Sample Counted, g.	Gram Atoms of Iodine Consumed Per Gram Cellulose	Intrinsic Viscosity, dl./g.	No. Av. D.P.	New Moles of Cellulose Formed During Grinding, $1/162(1/\overline{DP}_{ng} - 1/\overline{DP}_{no})$
1-T	0.0865	22 3/4	8,400	210	3.79	1.35×10^{-6}	0.64	82	7.4×10^{-5}
2-T	0.0965	21	11,100	322	3.70	1.79	0.62	79	7.7
3-T	0.0890	12	10,800	232	3.68	1.22	0.96	123	4.8
4-T	0.0950	--	12,200	136	3.48	0.72	1.34	172	3.3
5-T	0.0920	34	6,400	483	3.87	3.23	0.44	56	10.5
6-T	0.460	16 1/2	--	--	--	--	0.61	78	--
7-T	0.458	19	15,600	187	3.93	3.30	0.58	74	8.0
8-T	0.445	15 3/4	13,900	220	3.94	4.21	0.60	77	7.7
9-T	0.430	35 3/4	11,600	201	3.13	5.61	0.37	47	12.8
10-T	0.415	20	13,300	242	3.53	5.00	0.48	61	9.6
11-T	0.455	18	13,600	150	3.20	3.70	0.55	70	8.5
12-T	2.00	18	17,800	146	3.55	10.9	0.40	51	11.7
13-T	2.00	23 1/2	15,100	165	3.58	14.0	0.28	36	16.8
14-T	2.00	17 3/4	21,100	140	3.61	8.7	0.40	51	11.7
16-T	2.00	40	14,900	183	3.11	18.0	0.18	23	23.4
17-T	2.00	19	12,800	121	3.45	12.9	0.34	44	13.6
18-T	2.00	186	--	--	--	--	0.14	18	--
19-T	20.0	19	14,100	19	3.86	16.4	0.30	38	15.9
20-T	0	192	--	--	--	--	0.15	19	--

[a]This count has been corrected for background. The corresponding count for a blank run in which glucose was ground for 47 hr. in the presence of carbon tetrachloride containing 2.0 g. iodine per liter was less than 5 counts per min. (c.p.m.) above background. This count for a blank run in which cellulose was ground for 45 min. in the presence of iodine in carbon tetrachloride (2.0 g./l.) and then allowed to stand for 7 days prior to extraction was less than 10 c.p.m. above background.

TABLE II

THE GRINDING OF AIRDRY AND OVENDRY CELLULOSE IN CYCLOHEXANE

Run No.[a]	Iodine Concentration, g./l.	Milling Time, hr.	100 Sec. Counts on Cellulose Sample After Grinding: Total Slurry Prior to Extraction	100 Sec. Counts on Cellulose Sample After Grinding: Sample After Excess Iodine Has Been Extracted	Weight of Sample Counted, g.	Gram Atoms of Iodine Consumed Per Gram Cellulose	Intrinsic Viscosity, dl./g.	No. Av. $\overline{D.P.}$	New Moles of Cellulose Formed During Grinding, $1/162(1/\overline{DP}_{ng} - 1/\overline{DP}_{no})$
1-CA	2.0	26	13,100	112	3.47	11.8×10^{-6}	0.39	50	12.0×10^{-5}
2-CA	2.0	41	17,700	158	3.58	11.7	0.32	41	14.6
3-CA	2.0	40	14,900	182	2.90	19.2	0.23	29	20.8
4-CO	2.0	25.5	18,300	135	3.24	10.8	0.41	52	11.5
5-CO	2.0	20	22,100	113	3.16	7.4	0.44	56	10.6
6-CO	2.0	38	25,300	205	3.54	10.8	0.32	41	14.6
7-CO	0	18	--	--	--	--	1.15	147	--
8-CO	0	22.5	--	--	--	--	0.89	114	--
9-CO	0	29	--	--	--	--	0.71	91	--
10-CA	0	18	--	--	--	--	1.20	154	--
11-CA	0	23	--	--	--	--	1.09	140	--
12-CA	0	30	--	--	--	--	0.63	81	--
13-CA	0	188	--	--	--	--	0.15	19	--

[a] CA refers to airdry cellulose ground in cyclohexane.
CO refers to ovendry cellulose ground in cyclohexane.

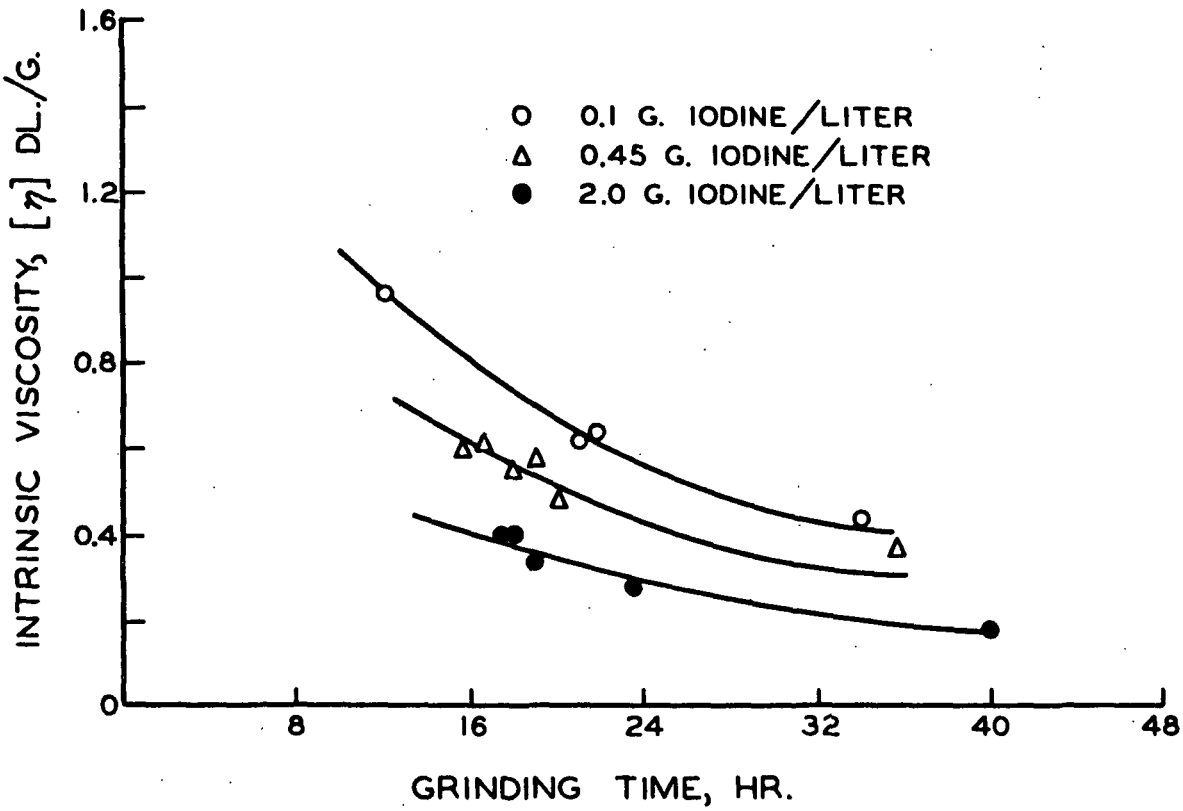

Figure 5. Cellulose Intrinsic Viscosity as a Function of Grinding Time for the Degradation of Cellulose in Carbon Tetrachloride

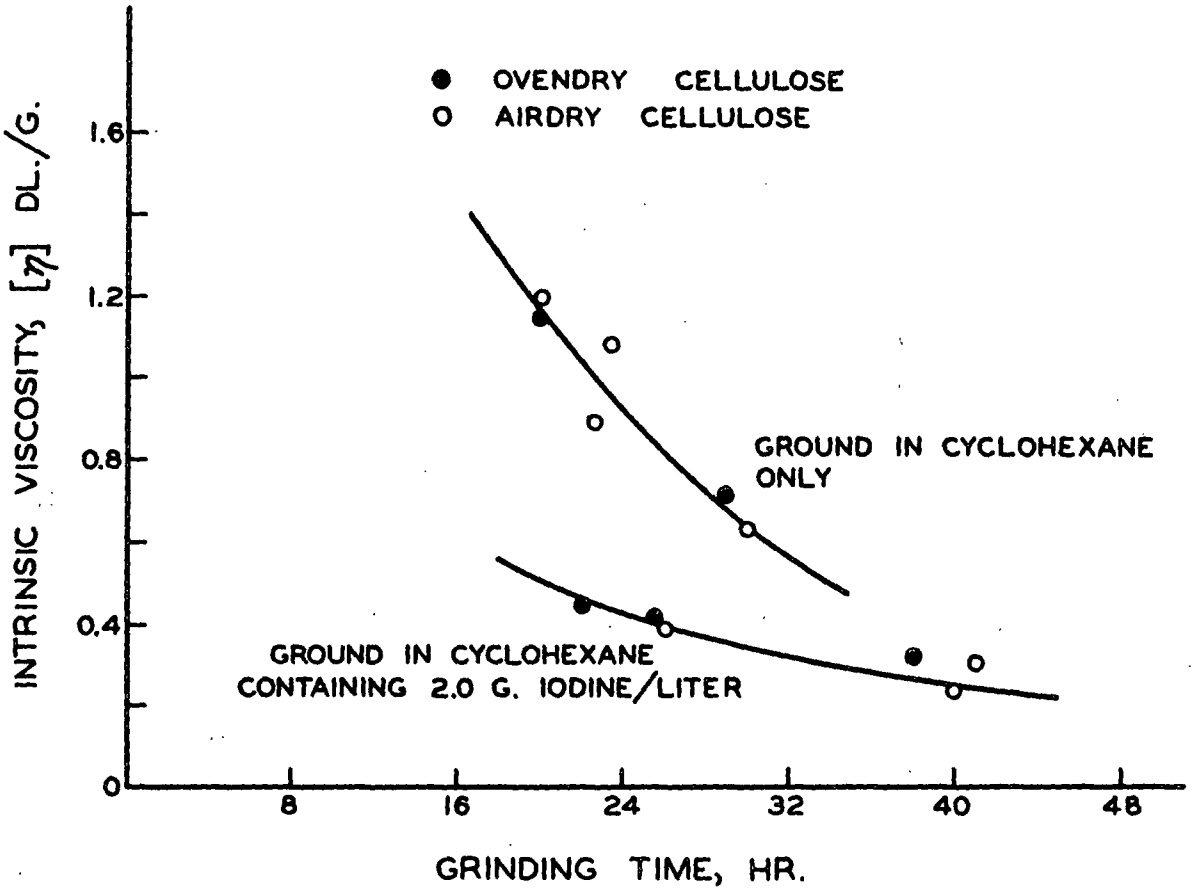

Figure 6. Cellulose Intrinsic Viscosity as a Function of Grinding Time for the Degradation of Cellulose in Cyclohexane

Since ESR spectra have established the presence of free radicals in a ball-milled cellulose sample, it may then be reasonably concluded that the iodine accelerates the degradation of cellulose during milling by preventing the recombination of at least some of the macroradicals which are formed. Under a nitrogen atmosphere, the likely fate of cellulose macroradicals formed during milling in the presence of an organic solvent would be recombination, chain transfer with the solvent, or disproportionation of radical pairs.

THE CORRELATION OF IODINE CONSUMPTION BY THE CELLULOSE AND THE ADDITIONAL MOLES OF CELLULOSE FORMED DURING GRINDING

By definition, the number average molecular weight of a cellulose sample is the total weight of the sample divided by the total number of moles of molecules it contains. Then, for 1-gram samples,

$1/\underline{M_n}$ = moles of cellulose present,

$1/\underline{M_{no}}$ = moles of cellulose present prior to mechanical degradation, and

$1/\underline{M_{ng}}$ = moles of cellulose present after mechanical degradation.

The number of new cellulose molecules formed during grinding is then given by

$$\frac{1}{\underline{M_{ng}}} - \frac{1}{\underline{M_{no}}} = \frac{1}{162}\left(\frac{1}{\underline{DP_{ng}}} - \frac{1}{\underline{DP_{no}}}\right).$$

Provided chain scission occurs primarily at the glycosidic links, two free radicals may be formed for each chain formed. Therefore, the moles of new cellulose molecules formed during grinding will be chemically equivalent to the moles of iodine consumed during grinding provided the iodine acts as an effective radical scavenger and the degradation proceeds with only free radicals being formed at the chain breaks.

The experimental results, plotted as iodine consumption by the cellulose versus the additional moles of cellulose formed during grinding, appear in Fig. 7. One important result shown here is that the iodine consumption is a function of iodine concentration prior to grinding over the range of from 0.1 to 2.0 grams per liter. This tends to confirm the hypothesis that the observed increase in the rate of degradation as the iodine concentration increases over this range (see Fig. 5) is due to the fact that more radicals are terminated by the iodine. Another interesting observation is that no significant differences can be detected between the data points for runs in which ovendry or airdry cellulose samples were ground with iodine in cyclohexane.

If we assume that chain scission in cellulose molecules due to mechanical grinding occurs primarily at the glycosidic links with two free radicals being formed at each chain break, then the slope of the iodine consumption-additional moles of cellulose formed during grinding plot indicates that, at most, only 5% of the free radicals formed during grinding are actually chemically combined with iodine. A number of explanations for this low value are given below:

1. The values for iodine consumption and/or the additional moles of cellulose formed during grinding are in error.

2. The degradation of cellulose is not completely mechanical in origin.

3. The iodine and cellulose free radicals, although they react, do not form stable addition compounds.

4. Oxygen or some other adventitious substance in the grinding system effectively competes with the iodine for free radicals.

5. Due to the heterogeneity of the system with which we have worked, iodine molecules are not always available for chemical combination with cellulose free radicals and other termination reactions occur.

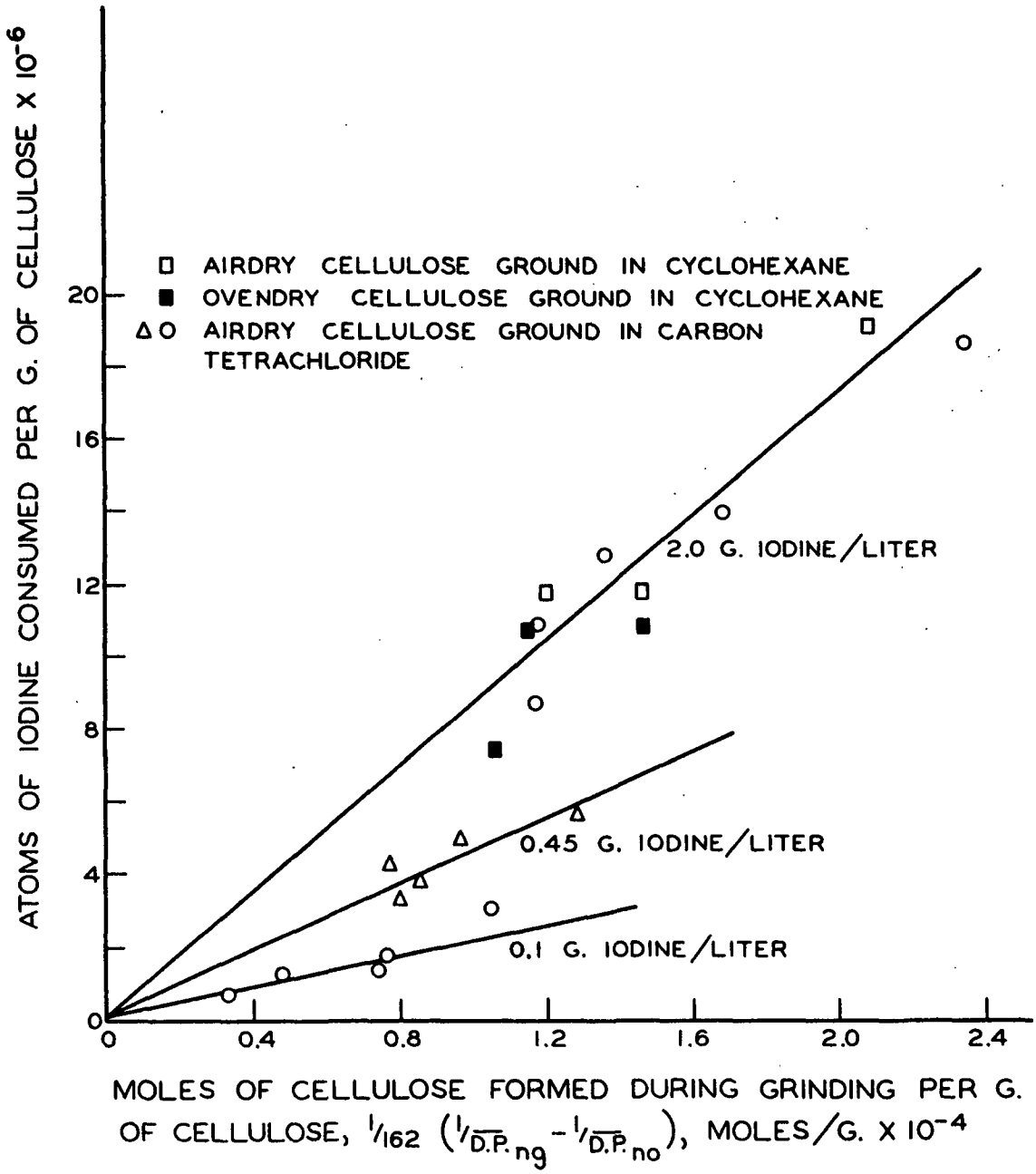

Figure 7. Iodine Consumption by Cellulose as a Function of the Additional Moles of Chains Formed During Grinding

6. The degradation is characterized by macroion as well as macroradical formation.

Each of these possibilities will be discussed in detail.

It is not thought that errors in the estimates of iodine consumption account in any way for the low results. Figure 19 in Appendix IV shows that for two samples, a slurry and a solution, iodine consumption is directly proportional to radioiodine count over the range of iodine concentrations and counts encountered in this investigation. Also, blank runs with glucose ground with iodine for 48 hours and cellulose ground for less than an hour with iodine and allowed to stand for about one week both indicate that no error in the estimate for iodine consumption will be encountered in the treatment of the sample after grinding provided there is no tendency for free iodine to be formed from reacted iodine. This is not likely.

As has been noted, the Mark-Houwink equation, $[\eta] = KM^{a}$, has been used to calculate cellulose number average molecular weights from cupriethylenediamine intrinsic viscosity data. All constants were evaluated by Immergut, et al. (39) using osmotic pressure-intrinsic viscosity data on a large number of unfractionated, partially fractionated, and fractionated cellulose samples. In a strict sense, however, this method may be used to calculate number average molecular weights of polymers only when the D.P. distribution does not change from sample to sample. Therefore, the probable errors involved in using such a correlation should be discussed.

The data of Immergut are shown in graphical form in Fig. 18 in Appendix III. If we let the y-value for a sample equal the ratio of the weight average molecular weight, calculated from intrinsic viscosity data of the nitrate in ethyl acetate,

to the number average molecular weight determined by osmometry, it may be seen that the points fall into three definite regions depending on the y-value of the sample. For y-values between 1.30 and 1.55, the number average $\overline{D.P.}$'s calculated using the correlation are 0 to 30% too high; for y-values between 1.15 and 1.30, the number average $\overline{D.P.}$'s calculated using the correlation are approximately correct; for y-values between 0.99 and 1.15, the number average $\overline{D.P.}$'s calculated using the correlation are 0 to 30% too low.

As long as the D.P. distribution of the cellulose does not change from sample to sample, the correlation should give good results for the number average $\overline{D.P.}$ on a comparable basis even if each $\overline{D.P.}$ is between 0 and 30% in error. However, during the mechanical degradation of cellulose, it may be expected that the polymer tends to become more homodisperse as the $\overline{D.P.}$ approaches the limiting $\overline{D.P.}$ Therefore, calculations on the moles of new molecules formed during grinding may be more than 30% in error if the D.P. distribution of the polymer sample goes from a high to a low y-value. It is fortunate that the $\overline{D.P.}$ of the unground cellulose is very large compared to the $\overline{D.P.}$'s obtained after grinding. As a result, the error in determining the number of new moles formed during grinding will be almost entirely the error in determining the number average molecular weight of the ground sample. The range of $\overline{D.P.}$'s for the ground samples is 23-172 with most results concentrated in the $\overline{D.P.}$ range of from 30 to 80. It is almost a certainty that large changes in the y-value do not occur over this limited molecular weight range.

The use of the correlation for molecular weights outside the range over which the constants were determined may be questionable, but the work of Staudinger and Eder (40) indicates no great error is involved. These investigators have studied the osmotic pressure molecular weight-viscosity relationship of severely degraded cellulose acetate and cellulose samples in the D.P. range of from 20 to 80. They

found that the viscosity constants determined for the degraded celluloses were almost the same as for higher molecular weight celluloses.

The viscosity and osmotic pressure molecular weight data of Staudinger and Eder have been tabulated in Table VII in Appendix III. The equivalent intrinsic viscosities in cupriethylenediamine for these samples have been calculated by assuming the viscosity number in cuprammonium hydroxide is equal to the intrinsic viscosity in cuprammonium (this is an excellent assumption for molecular weights in this range) and that the intrinsic viscosity in cupriethylenediamine is 1.54 times the intrinsic viscosity in cuprammonium hydroxide (41).

The calculated points are also shown in Fig. 18 in Appendix III. It may be seen that for a given intrinsic viscosity, the correlation gives results about 20% less than those calculated from Staudinger's data. Since this error is not significantly different from the errors in the correlation itself in the upper region, the correlation has been used to calculate the number of new moles of cellulose formed during grinding, realizing that the estimates may be up to 30% in error. An error of this magnitude could conceivably increase the value for the fraction of free radicals chemically combined with iodine from 5 to 7%.

It should be emphasized that the entire preceding discussion is based on the assumption that ball-milled cellulose does not contain units along the chain where rupture of single bonds has destroyed the ring structure. The opening of rings along the cellulose chain could certainly affect the values for K and a in the Mark-Houwink equation. Although Assarson, et al. (21) have isolated three, four, and five carbon fragments from the end groups of ball-milled cellulose, there is no evidence that this mechanical effect and the ring opening is restricted to the end groups (see p. 55).

It has already been stated in the previous section that high estimates for the moles of chains formed during the grinding due to secondary chemical degradation reactions involving iodine are unlikely because the limiting intrinsic viscosity is the same for samples ground in carbon tetrachloride with and without iodine.

There is a distinct possibility that instabilities of the reaction products between cellulose radicals and iodine account in part for the low results. Mechanical rupture of cellulose chains at a glycosidic link with the formation of two free radicals will result in the presence of an alkoxy ($R_3C\text{-}O\text{-}$) radical and an alkyl radical ($R\cdot$). Since no stable organic hypoiodite has ever been isolated (33), it is extremely unlikely that iodine will react with an alkoxy free radical to give a stable addition product. Provided that alkoxy radicals are relatively stable, only in situ combination with iodine is possible, and thus the figure of 7% for the fraction of free radicals that chemically combine with iodine may indeed be as high as 14%. Experimental evidence that in situ hypoiodites actually may be formed during the grinding of cellulose with iodine is presented in the next section.

The addition product from the reaction of cellulosic alkyl radicals and iodine may also be somewhat unstable since several alkyl organic iodides were observed to liberate free iodine when exposed to light over a period of time. The stability of the reaction product between cellulose radicals and iodine was therefore checked by grinding two cellulose samples with iodine and radioiodine under nitrogen and determining the iodine consumption on half of each sample immediately after grinding and on the other half 36 hr. after grinding. The results, shown in Table III, indicate there is no large difference between the two samples although the iodine concentration in each 36-hr. sample is about 10% lower than the corresponding sample treated immediately after grinding.

TABLE III

STABILITY OF THE CELLULOSE-IODINE REACTION PRODUCT OBTAINED AFTER THE MECHANICAL DEGRADATION OF CELLULOSE IN THE PRESENCE OF IODINE

Sample	Iodine Concn. During Grinding, g./l.	Time After Grinding that Counts Were Determined, hr.	100 Sec. Counts: Total Slurry After Grinding	100 Sec. Counts: Sulfuric Acid Layer After Extraction of Excess Iodine[a]	Indicated Consumption of Iodine by Cellulose, g.
1A	2.0	0	9,600	221	0.0139
1B	2.0	36	8,320	178	0.0128
2A	2.0	0	16,300	440	0.0162
2B	2.0	38	14,400	351	0.0146

[a]Corrected for background.

Even though it is possible that some oxygen remained in the jar after sealing, it is unlikely that it contributed greatly to the low results. Ceresa (15) has noted that when the concentration of polymer radicals is low, the presence of 0.1% oxygen or less may cause deactivation to be the predominant reaction. However, with high concentration of radicals as produced by vigorous mechanical degradation of high molecular weight polymers, deactivation by oxygen is considerably less and frequently immaterial. Evidence that oxygen does not act to any great extent as a radical-acceptor in this system is the fact that the curves formed by plotting the iodine consumption versus new moles of cellulose formed are linear. If oxygen was effectively competing with iodine for the cellulose free radicals, one would expect the curves to be concave upward since oxygen would tend to be consumed as the degradation progressed. Calculations show that if about 1% oxygen was present in the system and it was effectively competing with iodine for the cellulose free radicals, one would expect the curves to be concave upward since oxygen would tend to be consumed as the degradation progressed.

A factor which is difficult to evaluate but which may play no small part in the observed low results for iodine consumption during the mechanical degradation of cellulose is the heterogeneity of the system with which we have worked. Several reactions are likely to occur when a polymer is mechanically degraded in the presence of a radical-acceptor. The macroradicals formed may recombine, disproportionate in pairs, or be terminated or deactivated by the radical-acceptor.

The extent to which any one of these reactions takes place in a given system will depend to a degree on the ability of the radical-acceptor to compete effectively for macroradicals. Certainly, this ability is related to the probable fate of two macroradicals upon contact, recombination or disproportionation, and the availability of radical-acceptor molecules for reaction with polymer macroradicals. These contentions are illustrated by experimental data. Pike and Watson (7) have observed that rubber is degraded very slowly during mastication under nitrogen but the presence of radical-acceptors greatly accelerates the rate of degradation. Presumably, during mastication under nitrogen, the primary fate of rubber macroradicals is recombination, which is prevented by the presence of a radical-acceptor. In contrast, it has been observed (43, 9) that the presence of a radical-acceptor has no significant effect on the high rate of degradation of several vinyl polymers during mastication under nitrogen. It has been suggested that the observed differences between the rate of degradation of rubber and several vinyl polymers during mastication under nitrogen may be due to the fact that there is a much greater tendency for the vinyl polymer macroradicals to disproportionate upon contact rather than recombine. However, no experimental evidence supporting this contention has as yet been reported.

Although the presence of iodine results in an observable increase in the rate of cellulose degradation during vibratory grinding under nitrogen, the degradation

nevertheless proceeds very rapidly under a nitrogen atmosphere. Thus, it is possible that disproportionation of cellulose macroradicals and the heterogeneity of the cellulose-iodine system contribute to the low results for iodine consumption during the degradation of cellulose.

It is not thought that heterolytic scission of cellulose molecules accompanies the homolytic cleavage although there is little experimental justification for eliminating the possibility. If macroions are formed during the grinding of cellulose, it is almost certain that they are terminated by water molecules. Airdry cellulose contains about 10 times the required water to terminate the macroions formed by the heterolytic, mechanical degradation of cellulose from a $\overline{D.P.}$ of 1710 to a $\overline{D.P.}$ of 20. Therefore, one might expect differences in the rate of degradation and in iodine consumption during grinding between airdry and ovendry samples. However, Fig. 6 and 7 indicate that no such differences can be observed.

Finally, it is of interest to compare the results for the cellulose-iodine system with the results of Johnson (12), who has mechanically degraded polyisobutylene and polystyrene in the presence of iodine by the high-speed stirring of solutions of these polymers. His data indicate that only 40 to 63% of the polyisobutylene radicals and as few as 32% of the polystyrene radicals formed during the degradation are actually chemically combined with iodine. These low results were attributed to errors in number average molecular weights determined from viscosity data, the presence of oxygen in the system during degradation, and disproportionation of radical pairs in the system before combination with iodine. Johnson's results indicate that a value of about 15% for the fraction of cellulose radicals reacted with iodine during mechanical degradation may be quite reasonable when one considers the heterogeneous nature of the cellulose-iodine system investigated.

SOLVENT ANALYSIS AFTER GRINDING CELLULOSE IN THE PRESENCE OF IODINE IN CYCLOHEXANE AND TOLUENE

An interesting observation encountered during the work involving the grinding of cellulose in the presence of iodine and a solvent was the fact that a residual count remained in the iodine solvent after the excess iodine was extracted with aqueous sodium thiosulfate. This strongly indicated that an organic iodide was present in the solvent after grinding. Data showing this observed effect are tabulated in Table IV.

TABLE IV

IODIDE CONCENTRATION IN SOLVENT AFTER GRINDING CELLULOSE WITH IODINE

Grinding Time, hr.	Solvent	Iodide Concentration During Grinding, g./l.	100-sec. Counts: Total Slurry After Grinding	100-sec. Counts: Solvent After Thiosulfate Extraction[a]	Indicated Iodide Concentration in Solvent, g./l.
26	cyclohexane	2.0	13,100	116	1.8×10^{-2}
17.5	cyclohexane	2.0	20,500	119	1.2×10^{-2}
17.5	benzene	2.0	20,000	57	0.6×10^{-2}
16.75	toluene	2.0	17,700	60	0.7×10^{-2}
19	ethylbenzene	2.0	11,200	59	1.1×10^{-2}

[a]Corrected for background count which was usually about 30 c.p.m. and losses which occurred during extraction and drying.

These data indicate that the iodine that reacted with the solvent is an appreciable fraction of the iodine which reacts with the cell during grinding (see Table II).

The obvious explanation for the presence of an iodide in the solvent after the grinding of cellulose was that iodine had reacted directly with the solvent.

Perry and Feldman (44) have observed that iodine reacts to a limited degree with benzene, toluene, and ethylbenzene to form stable compounds. This explanation was rejected, however, when it was found that no significant radioactivity was found in cyclohexane or toluene after grinding glucose for 48 hours under the same conditions.

The possibility that atomic iodine present in the grinding system accounted for the halogenations was then investigated. If R:O:R represents a cellulose molecule which is homolytically ruptured in the presence of iodine and a solvent, SX, the following reactions may occur:

$$R{:}O{:}R \xrightarrow[\text{Energy}]{\text{Mechanical}} R{:}O\cdot + R\cdot$$

$$R\cdot + I_2 \longrightarrow RI + I\cdot$$

$$I\cdot + SX \longrightarrow HX + S\cdot$$

$$S\cdot + I_2 \longrightarrow SI + I\cdot$$

However, the prospects for solvent halogenation by iodine atoms are not good. Walling (32) points out that such reactions are unfavorable from both an enthalpy and free energy viewpoint and have not been observed.

It was then thought that perhaps chain transfer reactions involving cellulose macroradicals and the solvent accounted for the radioactivity in the solvent. If R· represents a cellulose free radical and SX the solvent, then the reactions involved would be

$$R\cdot + SX \longrightarrow RX + S\cdot$$

$$S\cdot + I_2 \longrightarrow SI + I\cdot$$

Numerous studies on the chain transfer reactions occurring in polymerizing monomer-solvent systems have shown that the reactivity of a solvent molecule to a polymeric

free radical is centered in a univalent atom on the most substituted carbon atom. The nature of the substituents and steric factors govern the chain transfer rates. If M represents a monomer molecule, M· a polymerizing macroradical, and SX a solvent molecule, two reactions that occur in a system where M is being polymerized in the presence of SX are

$$M\cdot + M \xrightarrow{k_p} MM\cdot$$

$$M\cdot + SX \xrightarrow{k_t} MX + S\cdot$$

where

k_t = the rate of chain transfer and

k_p = the rate of polymerization.

A chain transfer constant, C, is defined as k_t/k_p. It is of interest to compare the amount of iodide present in a given solvent after grinding cellulose with iodine (from Table IV) with the chain transfer constant for this solvent during the polymerization of styrene and methyl methacrylate. This comparison appears in Table V.

TABLE V

COMPARISON OF SOLVENT CHAIN TRANSFER CONSTANTS WITH THE IODIDE CONCENTRATION IN THE SOLVENT AFTER GRINDING CELLULOSE WITH IODINE

Solvent	Grinding Time, hr.	Iodide Concn. After Grinding, g./l.	Chain Transfer Constants x 10^5		
			Styrene, 100°C. Schultz (45, 48)	Styrene, 100°C. Suess (46-48)	Methyl Methacrylate, 80°C. (49)
Cyclohexane	17.5	1.2×10^{-2}	3.1	--	1.0
Benzene	17.5	0.6×10^{-2}	3.1	4.2	0.75
Toluene	16.75	0.7×10^{-2}	5.3	7.2	5.25
Ethylbenzene	19	1.1×10^{-2}	14	23	13.5

If chain transfer reactions account for the presence of iodide in the solvent after grinding with iodine, the amount of iodide present should be related to the chain transfer constant of the particular solvent and one should expect significantly more iodide in the solvent after grinding in ethylbenzene than after grinding in cyclohexane. Since the data indicate that there is somewhat less iodide formed when cellulose is ground in ethylbenzene than when cellulose is ground in cyclohexane, it is thought that chain transfer reactions do not account for the formation of iodide in the solvent during grinding.

The use of chain transfer constant data for polymerizing monomer-solvent systems to exclude the possibility that chain transfer reactions do not account for halogenation of the solvent in the cellulose system may be criticized on the basis that these data were obtained using different radicals in true solutions at much higher temperatures. However, the data tabulated by Walling (55) indicate that neither temperature differences or differences in the type of attacking radical will change the idea that ethylbenzene should exhibit a significantly larger chain transfer constant than benzene or cyclohexane in solution. This is no doubt due to the well-known fact that the C-H bond strength for cyclohexane is higher than that for a benzyl or β-phenethyl C-H bond.

There is a possibility that a steric factor, which reflects the fact that in order to react it may be necessary for a radical and solvent molecule to collide in some particular relative orientation, affects chain transfer constants. It is also conceivable that this factor changes as one goes from a true solution to a heterogenous system. Certainly if this is true, one might expect a cyclohexane molecule with a number of reactive C-H bonds to be less affected by a changing steric factor than an ethylbenzene molecule which has just two reactive C-H bonds. Whether or not such a steric effect could overcome the greater reactivity of phenethyl C-H bonds compared to cyclohexyl C-H bonds would be strictly conjecture, however.

It has already been noted that there is a possibility of alkoxy radicals being formed during the mechanical degradation of cellulose and the combination of iodine with alkoxy radicals to give a stable product is doubtful because no stable organic hypoiodite has ever been isolated. However, hypoiodites have been formed in situ and are known to be effective halogenating agents. To investigate the possibility that a hypoiodite type of structure accounted for the solvent halogenation during the grinding of cellulose, the halogenation products formed in cyclohexane and toluene were investigated.

After reduction in volume from 600 to 12 cc. by distillation, the solvent from two runs in which cellulose was ground in the presence of cyclohexane containing 2 g. of iodine per liter was gas chromatographed. The resulting thermal conductivity versus retention time curve appears in Fig. 8. Figure 9 shows thermal conductivity versus retention time curves for cyclohexane and a known solution containing 5 microliters of cyclohexyl iodide in 50 ml. of cyclohexane determined under the same conditions. Comparing the two, it may be seen that there is a thermal conductivity peak in the unknown comparable to the cyclohexyl iodide peak in the known.

To establish with certainty that this unknown compound, which was chromatographically indistinguishable from cyclohexyl iodide, was indeed cyclohexyl iodide, several fractions were collected in cyclohexane as the material passed from the gas chromatograph and its ultraviolet absorption spectrum was determined. The results, shown in Fig. 10, clearly indicate that the ultraviolet absorption of the unknown compound is comparable to those for known solutions of cyclohexyl iodide in cyclohexane. Maximums at about 260 mμ are observed. Haszeldine (50) has reported a maximum absorption at 260 mμ for cyclohexyl iodide in light petroleum solution. Thus, the formation of cyclohexyl iodide during the grinding of cellulose in the

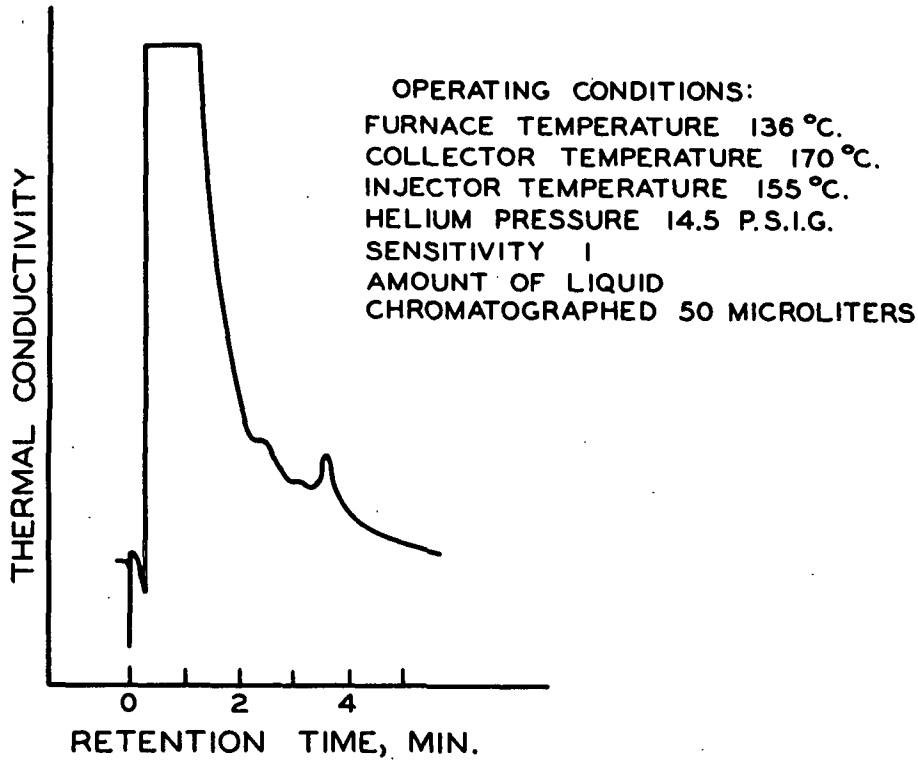

Figure 8. Gas Chromatogram of Cyclohexane Used to Grind Cellulose With Iodine After Concentration From 600 to 12 ml.

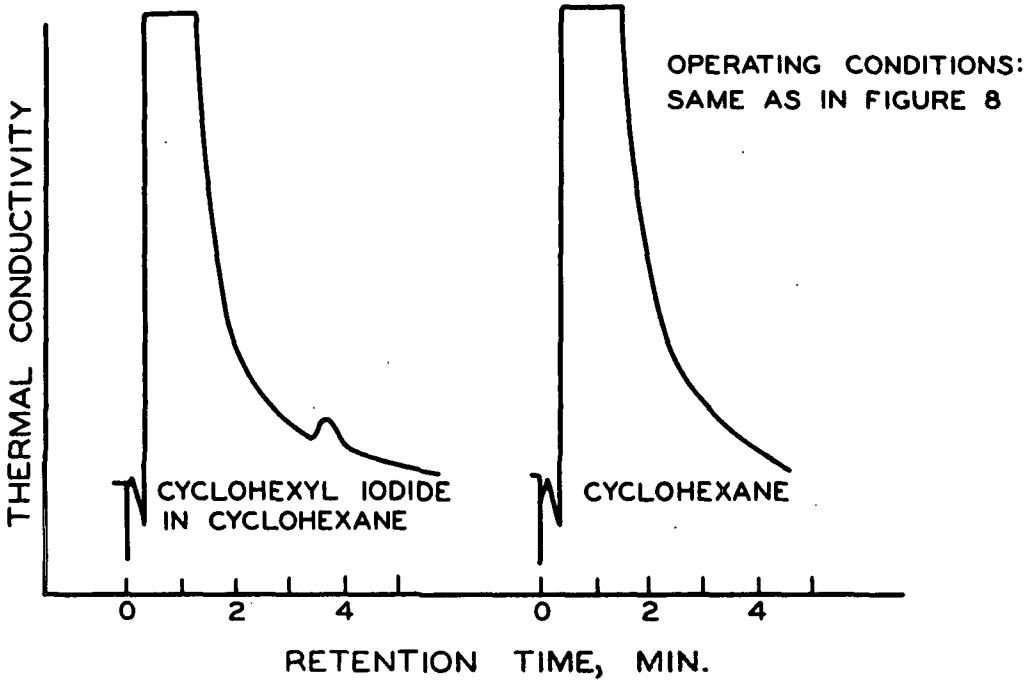

Figure 9. Gas Chromatograms of Cyclohexane and a Known Solution Containing 100 Microliters of Cyclohexyl Iodide per Liter of Cyclohexane

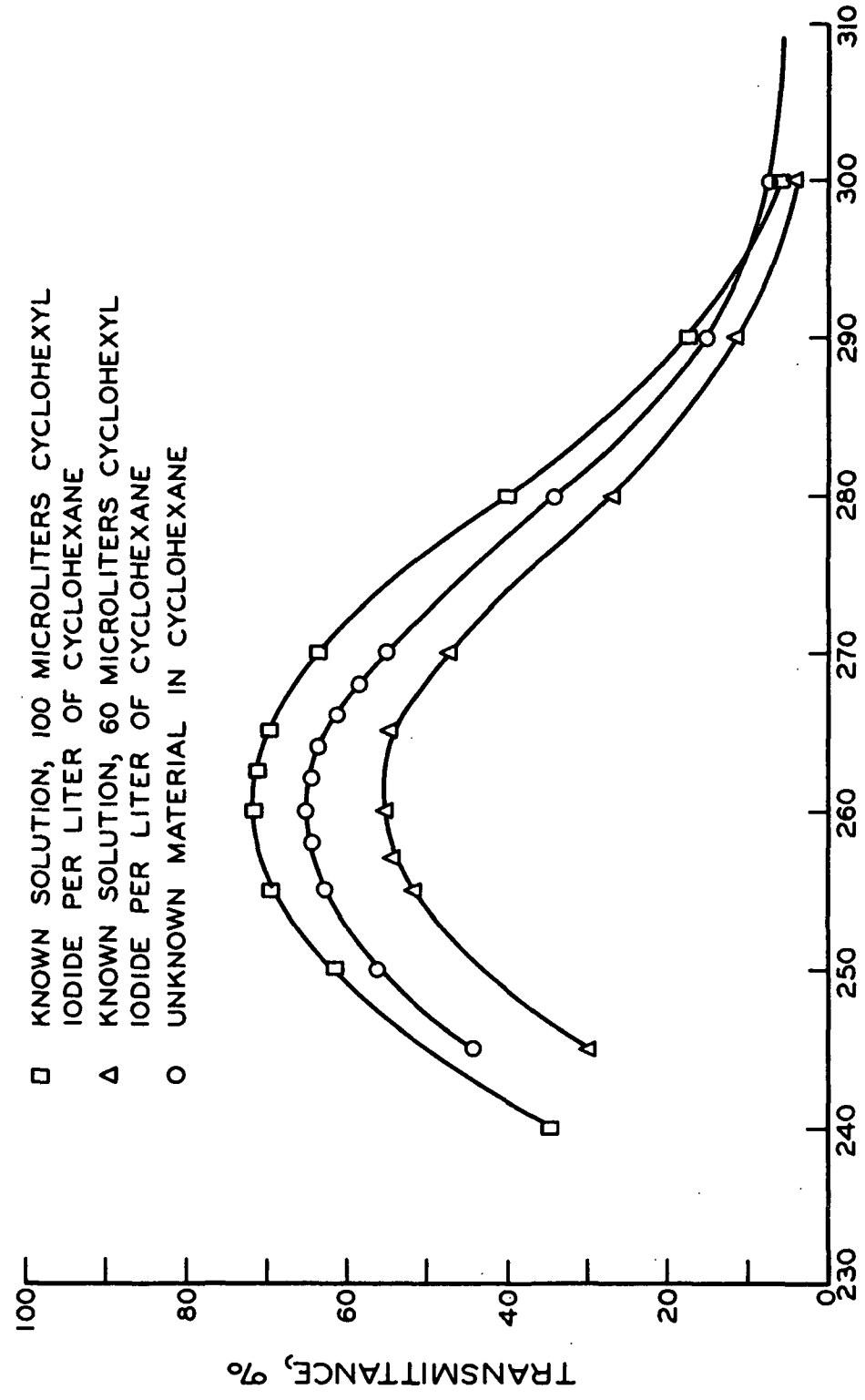

Figure 10. Ultraviolet Spectra of Cyclohexyl Iodide and Unknown Substance in Cyclohexane

presence of iodine and cyclohexane has been confirmed. Similarly, Fig. 11 through 13 show that benzyl iodide is present after grinding cellulose with iodine in toluene.

The halogenation of the aliphatic hydrocarbon and the aromatic hydrocarbon in the side chain strongly suggests that the halogenation reaction is characterized by a radical rather than an ionic reaction. Such a reaction must involve more than simple dissociation of the hypoiodite (R_3C-O-I) into R_3C-O· and I· because, as already noted, atomic iodine is not capable of direct solvent attack. A more complex reaction involving cellulose free radicals and/or free iodine may certainly be possible.

It is interesting to note that Hammond (54) has studied the decomposition of benzoyl peroxide in the presence of iodine in benzene and chlorobenzene and has noted that a large degree of solvent halogenation occurs. He has ascribed the halogenation to a benzoyl hypoiodite intermediate and states that the substitution may be either ionic or radical. Since there is no evidence that a hypoiodite can halogenate by a radical mechanism, one certainly cannot dismiss the possibility that halogenation occurs through a chain transfer reaction. However, it is presently felt that a chain transfer mechanism is less likely than a mechanism involving a hypoiodite. It should be noted that, in either case, the low results for iodine can be partially explained.

The idea that alkoxy radicals are formed during the grinding of cellulose forms the basis for an alternative theory to account for the fact that the ball-milling of cellulose can actually rupture carbon-carbon bonds within the ring (21). This has been attributed to actual mechanical cleavage of carbon-carbon bonds in the ring, but certainly such reasoning can be criticized on the basis that a cellulose molecule subjected to a shear force will almost certainly break at the weakest point, the freely rotating glycosidic link, rather than in the stable, six-membered ring.

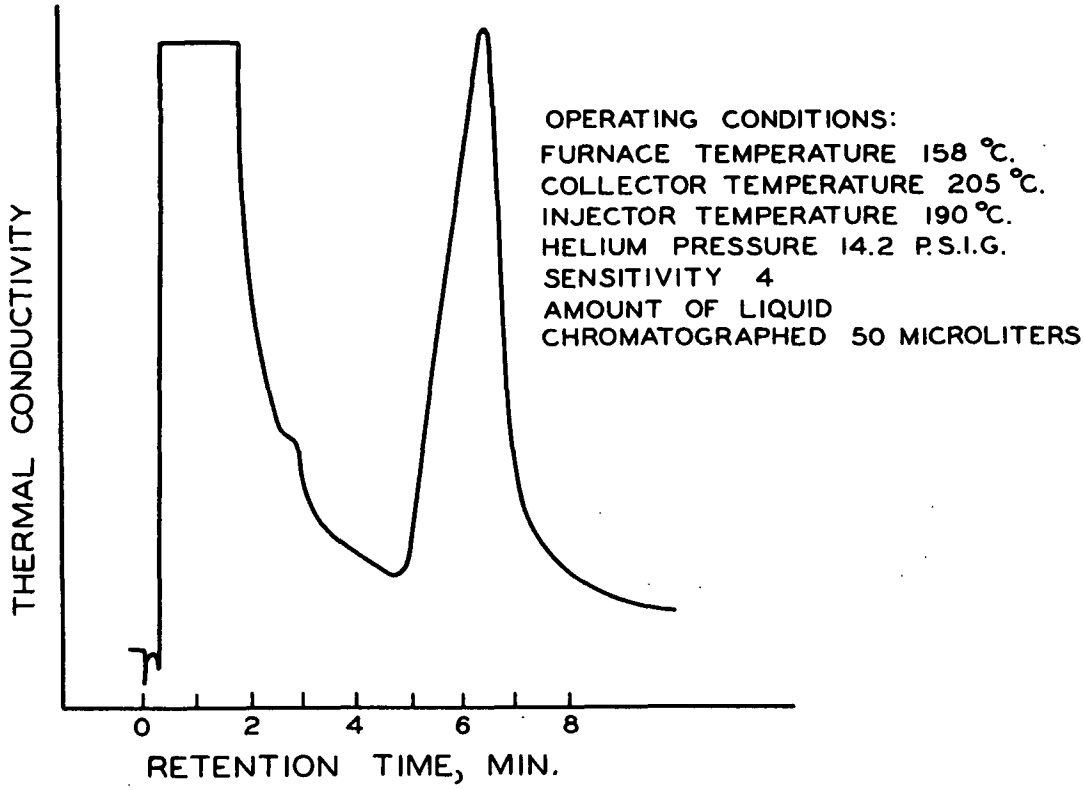

Figure 11. Gas Chromatogram of a Known Solution Containing Benzyl Iodide in Toluene

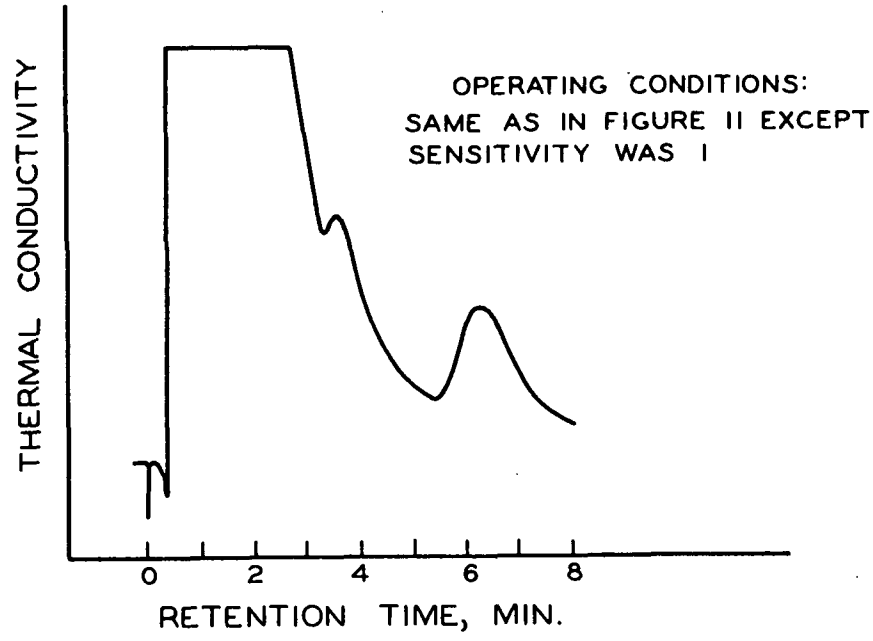

Figure 12. Gas Chromatogram of Toluene Used to Grind Cellulose with Iodine After Concentration from 600 to 4 ml.

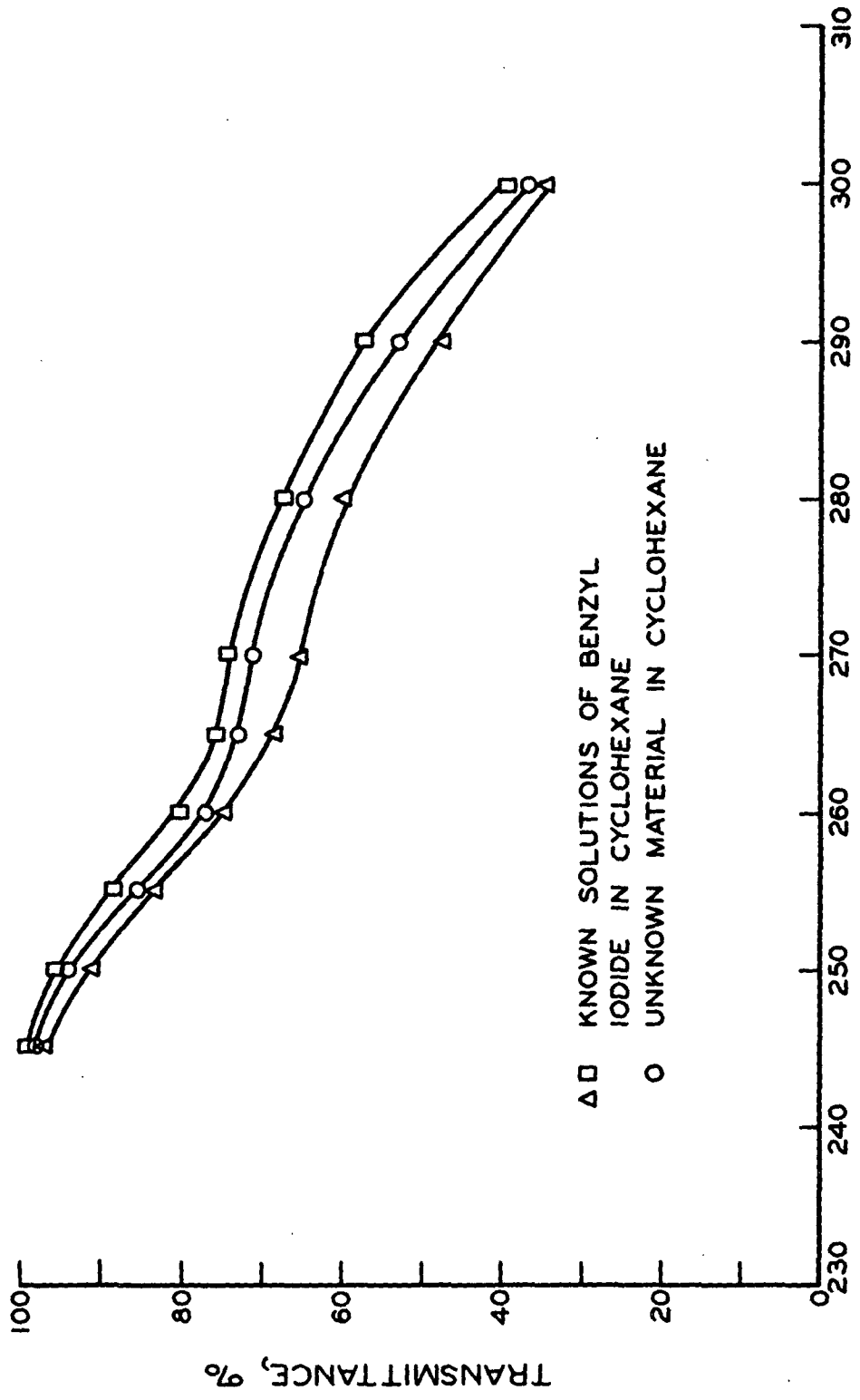

Figure 13. Ultraviolet Spectra of Benzyl Iodide and Unknown Substance in Cyclohexane

It is of interest that alkoxy free radicals are known to decompose by carbon-carbon bond fission as follows (22):

$$R - R'CHO\cdot \longrightarrow R\cdot + R'CHO$$

$$\text{or } R'\cdot + RCHO.$$

Also, when alkoxy radicals derived from alicyclic alcohols decompose, carbon-carbon fission in the ring may occur. For example, cyclohexoxyl radicals decompose to give $\cdot CH_2(CH_2)_4CHO$. Therefore, it is suggested that reactions involving carbon-carbon bond fission of cellulosic alkoxy radicals formed during milling accounts for the isolation of three, four, and five carbon fragments from the end groups of a ball-milled cellulose sample.

SUMMARY AND CONCLUSIONS

The mechanism of the mechanical degradation of airdry cellulose by vibratory grinding has been investigated. From electron spin resonance spectra of a ball-milled cellulose sample, it has been established that the degradation is characterized by the formation of free radicals.

The effect of iodine on the rate of mechanical degradation of airdry and ovendry cellulose suspensions in carbon tetrachloride and cyclohexane was studied. It was found that the rate of degradation is observably increased as the iodine concentration increases from 0 to 2.0 g./l. It is suggested that the iodine increases the rate of degradation by preventing the recombination of at least some of the cellulose radicals formed during grinding.

The extent to which a mechanically initiated free radical degradation mechanism occurs during the ball-milling of cellulose was studied by grinding cellulose in the presence of a radical-acceptor and determining the consumption of the radical-acceptor by the cellulose. For this purpose, iodine which contained a small amount of iodine-131 to provide a radiochemical method of analysis was employed. Assuming that two free radicals are formed at each chain break, it was shown that only about 5% of the macroradicals present during milling, as estimated from decreases in intrinsic viscosity, are actually chemically combined with iodine.

It is not thought that the low values for iodine consumption during the grinding of cellulose indicates that heterolytic, mechanical cleavage of bonds occurs along with homolytic cleavage. One reason is that iodine consumption as a function of the degree of degradation is the same for airdry and ovendry cellulose samples. Another reason is that because of possible errors in the experimentally determined number average molecular weights and the probable instability of the reaction product

formed between iodine and alkoxy radicals, it is conceivable that as many as 10 to 15% of the radicals formed actually react with iodine. It is thought that rapid disproportionation reactions between pairs of cellulose radicals and the heterogeneity of the cellulose-iodine system prevent further combination of iodine with cellulose macroradicals.

It was established that benzyl iodide and cyclohexyl iodide were formed when cellulose was ground with iodine in toluene and cyclohexane, respectively. In the case of cyclohexane, nearly as much iodine reacted with the solvent as reacted with the cellulose. Although it is possible that chain transfer reactions involving cellulose radicals and the solvent account for the halogenation of the solvent, it is felt that the halogenation is more likely due to a hypoiodite structure formed by the reaction of alkoxy radicals with iodine.

The rupture of glycosidic links in cellulose during milling to form alkoxy radicals suggests an alternative explanation for the formation of three, four, and five carbon fragments at the end groups of ball-milled cellulose. This has been attributed to actual mechanical rupture of carbon-carbon bonds in the ring. However, cyclic alkoxy radicals are known to decompose by carbon-carbon bond fission within the ring and it appears likely that such a reaction could occur during the milling of cellulose.

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APPENDIX I

CHARACTERIZATION OF THE ORIGINAL CELLULOSE SAMPLE

DEGREE OF POLYMERIZATION

Two random samples, about one gram each, were nitrated according to the method of Bennett and Timell (51). The linters were cooled to -30°C. and a nitrating mixture, prepared by adding fuming nitric acid to acetic anhydride at -30°C., was added with stirring. After three hours, the mixture was poured into chilled water (ca. 5°C.), washed with more chilled water until neutral to methyl red and stabilized in methanol overnight.

The viscosity of the nitrated linter samples as a function of concentration was determined in ethyl acetate solution using two Cannon dilution viscometers. The intrinsic viscosity, $[\eta]$, was obtained by extrapolating the plot of $\log \eta_{sp}/c$ versus c to zero concentration according to the Martin equation:

$$\log (\eta_{sp}/c) = \log [\eta] + K[\eta]c$$

where

η_{sp} = specific viscosity = $t/t_o - 1$

t = solution time through the viscometer

t_o = solvent time through the viscometer

$[\eta]$ = intrinsic viscosity

K = constant, and

c = concentration, g./100 ml.

The intrinsic viscosity was corrected for shear rate (see next section) and the degree of polymerization was determined from the correlation of Immergut, et al. (39):

$$[\eta] = 0.38 \times 10^{-4} M^{1.03}$$

where

$[\eta]$ = intrinsic viscosity, dl./g. and

$\underline{M}$ = number average molecular weight.

This relationship is good for nitrogen contents of 13.74 to 13.98% and number average molecular weights of approximately 25,000 to 1,000,000. The $\overline{D.P.}$ was found to be 1710.

DEGREE OF POLYMERIZATION DISTRIBUTION

The nitrated linters were fractionated by a method similar to that of Timell (52). Approximately 0.70 g. of the nitrate was dissolved in 410 ml. of acetone and 135 ml. of a 2:1 acetone to water mixture was added with vigorous agitation. Acetone was then removed by a stream of air with continuous stirring. When sufficient precipitate had formed, the contents were removed from the fractionating flask and centrifuged. The supernatant liquid was returned to the fractionating flask and the precipitate was removed from the centrifuge bottles by washing with methanol. The individual fractions were dried under a stream of air and weighed.

Intrinsic viscosities were obtained for all fractions. For high molecular weight nitrocellulose, Immergut, et al. (39) point out that the intrinsic viscosity is a function of the rate of shear. Therefore, the shear dependence of intrinsic viscosity was determined using the two Cannon dilution viscometers and a special Cannon shear dependence, dilution viscometer. For this special four bulb viscometer,

$$\overline{G} = \frac{8\underline{V}}{3\,\underline{r}^3\,\underline{t}} = \frac{1.062}{\underline{t}} \times 10^5$$

where

$\bar{G}$ = the mean shear rate for each bulb

V = volume of the bulb

r = radius of the capillary from each bulb, and

t = efflux time from each bulb.

No significant difference was observed between intrinsic viscosities obtained using the two standard viscometers. However, a significant dependence of intrinsic viscosity on shear rate was found for fractions with an intrinsic viscosity greater than about 12 dl./g. when the special shear viscometer was used. Therefore, a plot of $[\eta]_{\bar{G}=0}$ (obtained by extrapolating a log η_{sp}/c versus c curve to zero concentration) versus the observed $[\eta]$ was made using four selected fractions. The results are shown in Fig. 14. The remaining intrinsic viscosities were corrected for shear rate using this plot. It was assumed that because of the high nitrogen content of the original sample, 13.95%, all fractions had the same nitrogen content. The dependence of intrinsic viscosity on nitrogen content is well known (39).

The results for the fractionation experiment are tabulated in Table VI. The results plotted as integral and differential distribution curves appear in Fig. 15 and 16.

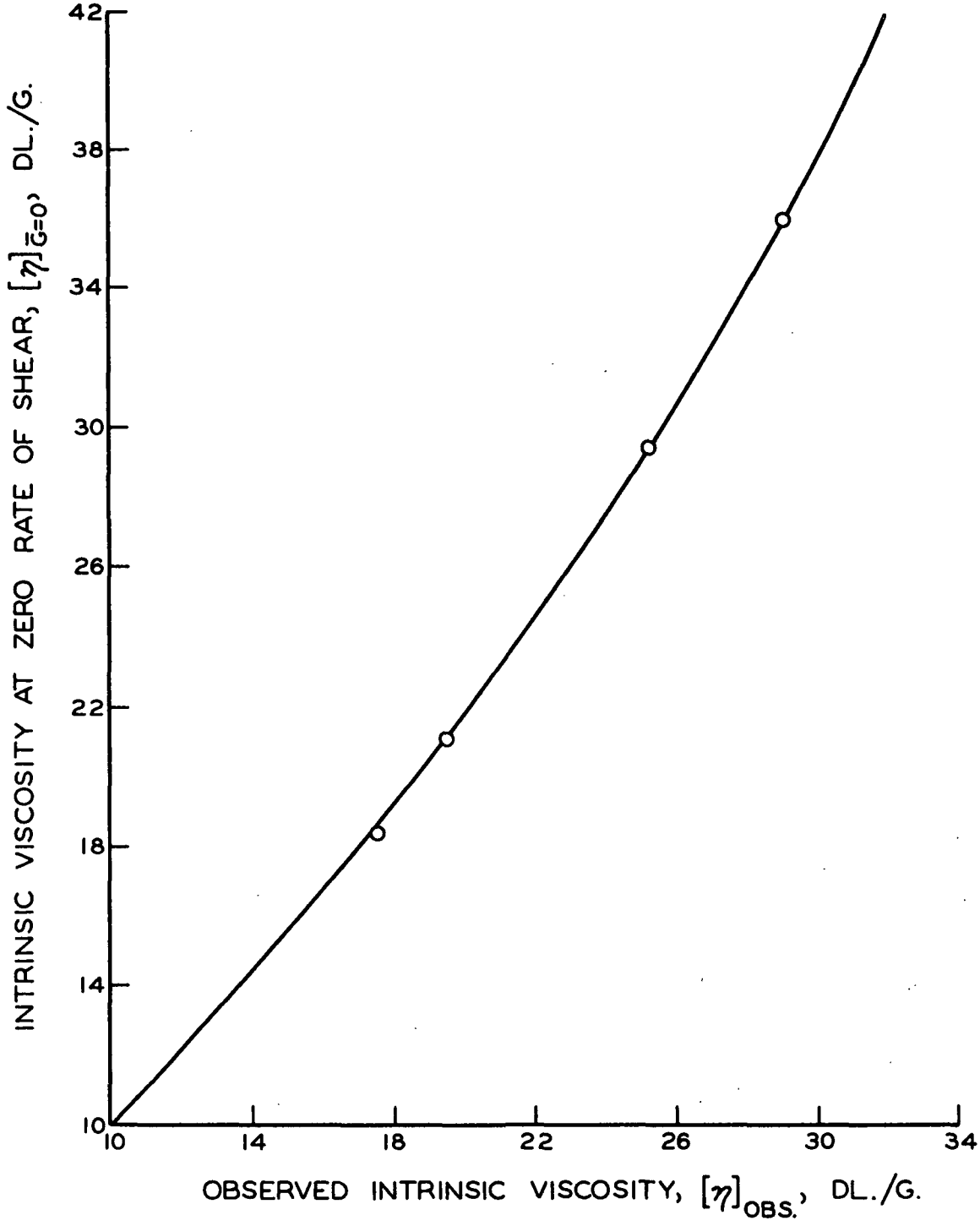

Figure 14. Shear Dependence of Cellulose Nitrate Intrinsic Viscosity in Ethyl Acetate

TABLE VI

FRACTIONATION DATA ON THE ORIGINAL CELLULOSE SAMPLE

Fraction	Cumulative Weight, g.	Cumulative Weight, %	Observed Intrinsic Viscosity, dl./g.	Intrinsic Viscosity for Zero Shear Rate, dl./g.	$\overline{D.P.}$
1	0.0854	12.7	32.8	43.7	2540
2	0.2318	31.9	30.0	37.7	2280
3	0.2722	40.6	29.1	36.0	2180
4	0.3150	47.0	28.0	34.0	2080
5	0.3965	59.1	25.3	29.5	1770
6	0.4900	73.1	19.7	27.5	1250
7	0.5568	83.2	17.6	18.6	1160
8	0.6111	89.7	12.5	12.7	850
9	0.670	100	5.0	5.0	340

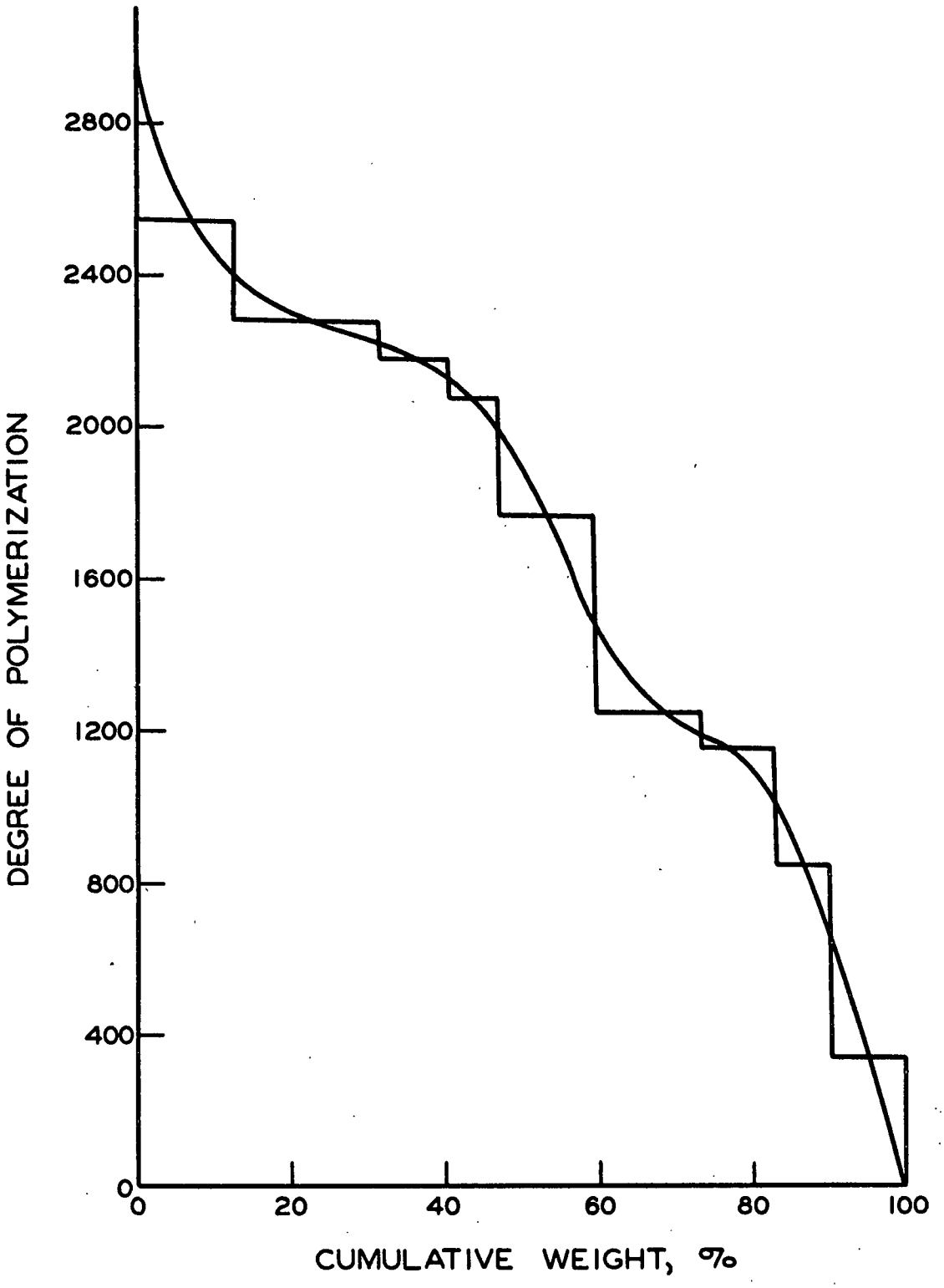

Figure 15. Integral Distribution for Nitrated Cotton Linters

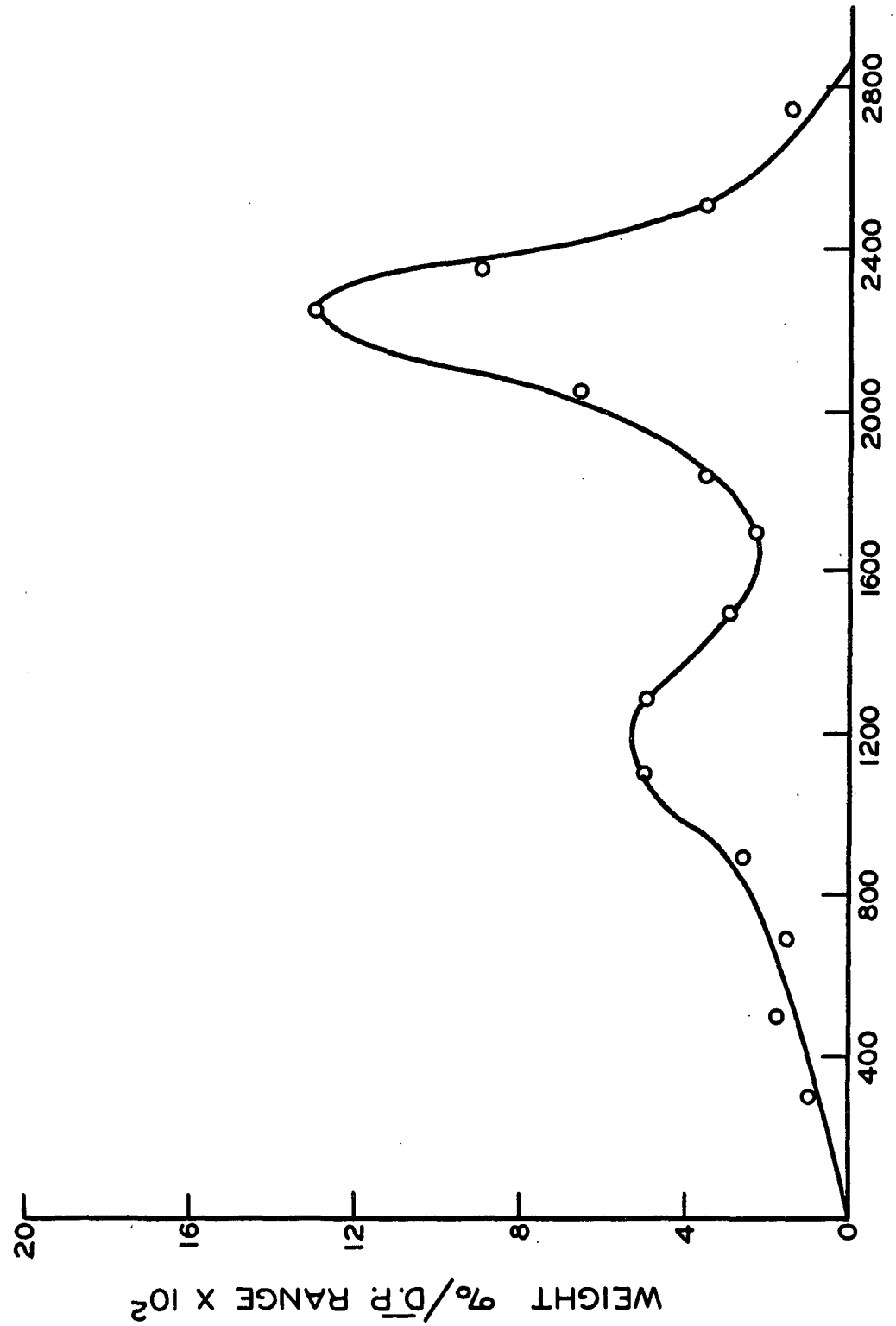

Figure 16. Frequency Distribution Curve for Nitrated Cotton Linters

APPENDIX II

DETERMINATION OF THE BEER'S LAW CURVE FOR IODINE IN CARBON TETRACHLORIDE

Two standard solutions containing weighed amounts of iodine in carbon tetrachloride (about 0.5 g./l.) were prepared. These solutions were then diluted volumetrically to give four solutions with iodine concentrations in the range of from 0.03 to 0.110 g. per liter. The transmittance of each of these solutions was determined against carbon tetrachloride in one cm. Corex cells at 520 mμ using the Beckman model DU spectrophotometer. The slit width was 0.02 mm. Results, plotted as the log of the per cent transmittance versus iodine concentration, appear in Fig. 17.

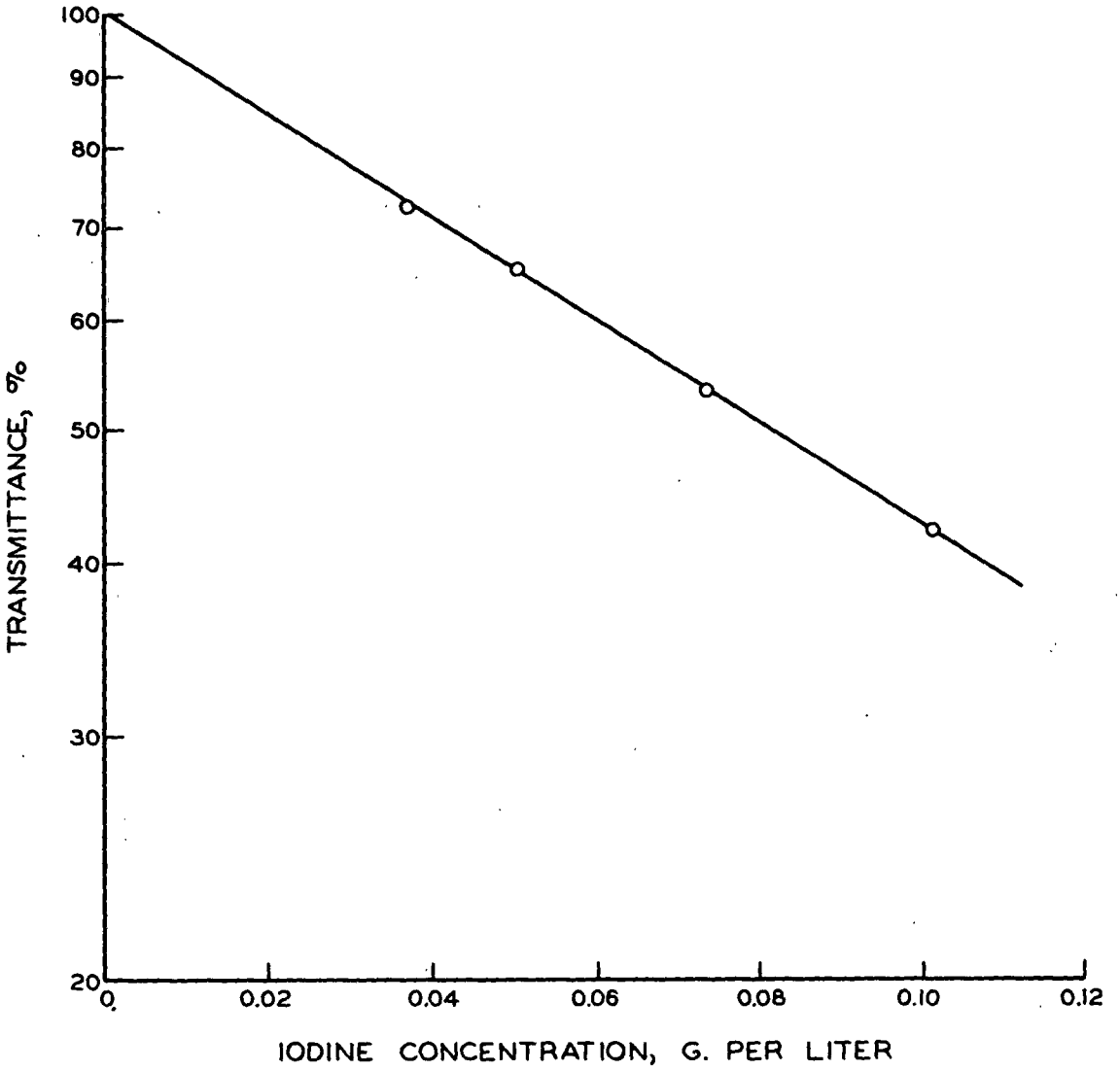

Figure 17. Beer's Law Curve for Iodine in Carbon Tetrachloride

APPENDIX III

THE CORRELATION OF INTRINSIC VISCOSITY IN CUPRIETHYLENE-DIAMINE AND OSMOTIC PRESSURE MOLECULAR WEIGHT FOR A NUMBER OF CELLULOSE SAMPLES

The intrinsic viscosity and osmotic pressure molecular weight data used by Immergut in determining the curve shown in Fig. 18 may be found in the original reference (39). The data of Staudinger and Eder (40), used to extrapolate the curve to low molecular weights appears in Table VII.

TABLE VII

OSMOTIC PRESSURE NUMBER AVERAGE MOLECULAR WEIGHT AND VISCOSITY DATA FOR HIGHLY DEGRADED CELLULOSE SAMPLES

Osmotic Pressure $\overline{D.P.}$ for Cellulose Acetate	Cellulose Viscosity Number in Cuprammonium Hydroxide, η_{sp}/c, dl./g.	Cellulose Intrinsic Viscosity in Cupriethylenediamine, $[\eta]$, dl./g.[a]
54	0.284	0.44
39	0.202	0.31
30	0.156	0.24
20	0.117	0.18

[a] Determined as $(1.54)(\eta_{sp}/c)_{Cuox}$

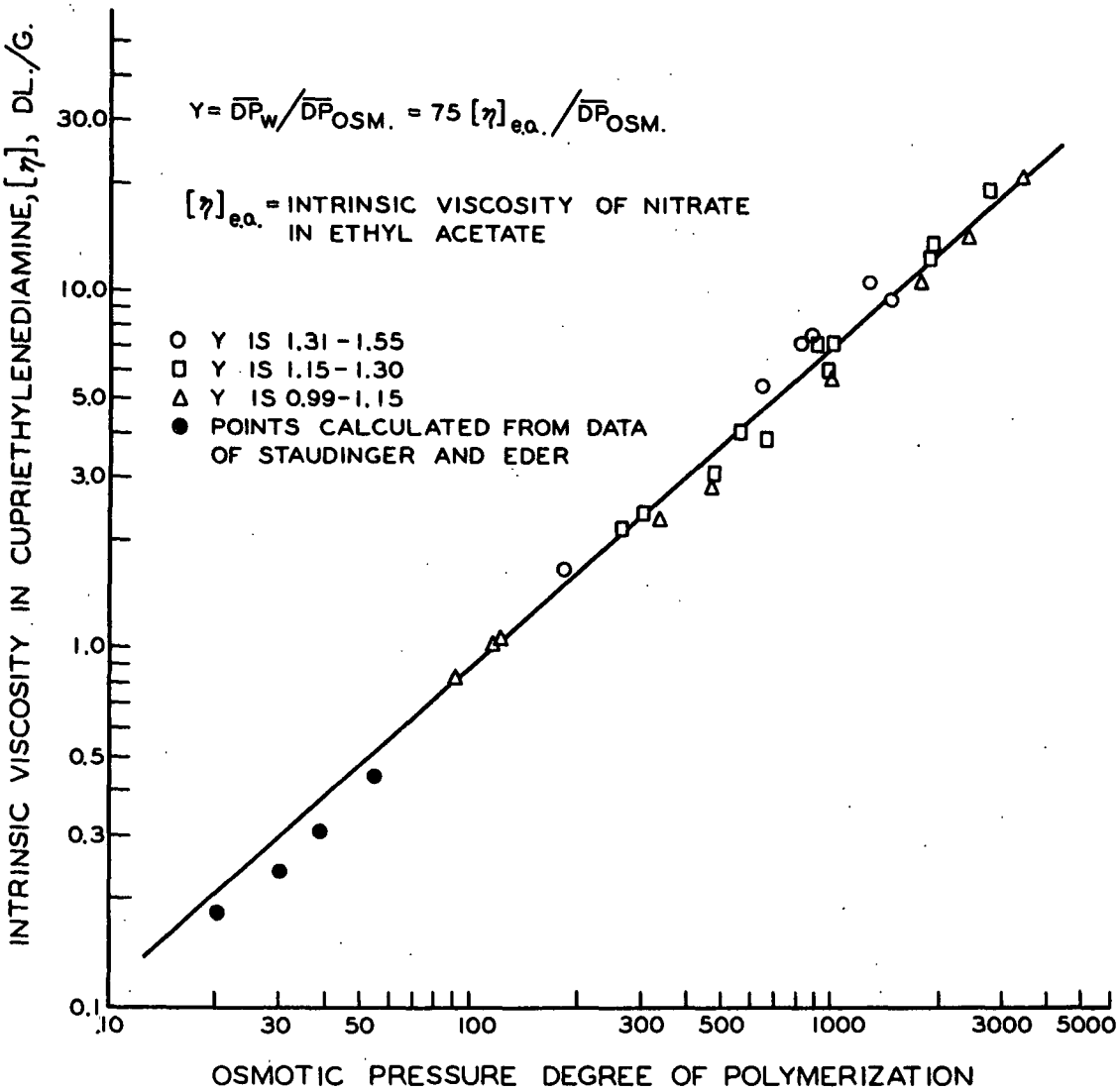

Figure 18. The Correlation of Intrinsic Viscosity in Cupriethylenediamine and Osmotic Pressure Molecular Weight for a Number of Cellulose Samples

APPENDIX IV

THE ACCURACY OF THE RADIOCHEMICAL METHOD FOR DETERMINING IODINE CONCENTRATIONS

The proportionality between iodine concentration and radioiodine count has been established. This was accomplished by counting two 300-ml. samples containing 2 g. of iodine per liter of methanol and enough radioiodine to give a count of about 15,000 c.p.m. and then counting successive volumetric dilutions of these samples. One sample contained only the iodine and radioiodine in methanol; the other also contained 5 g. of ground cellulose. Counts below 5,000 counts per 100 sec. were corrected for background.

The results, plotted as log of the radioiodine count versus log of the iodine concentration in Fig. 19, clearly show the proportionality between radioiodine count and iodine concentration.

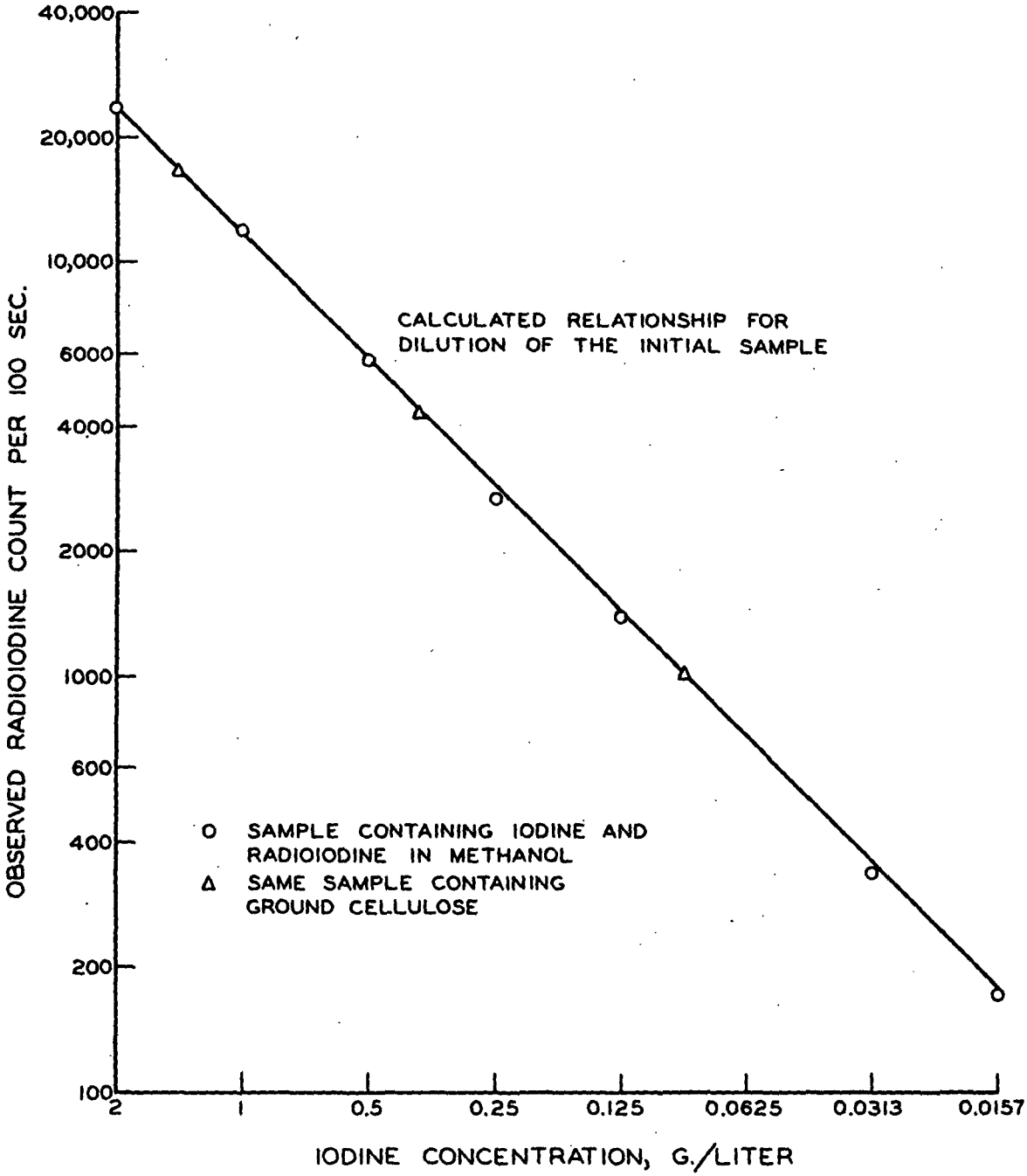

Figure 19. Observed Count from Radioiodine-131 as a Function of Iodine Concentration in a Particular Sample